ANALYSIS OF SELECTED LEAD-FREE SOLDERS BY OPTICAL EMISSION SPECTROSCOPY

YEE CHUNG LEE

FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2014

ANALYSIS OF SELECTED LEAD-FREE SOLDERS BY OPTICAL EMISSION SPECTROSCOPY

YEE CHUNG LEE

RESEARCH REPORT SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE (ANALYTICAL CHEMISTRY & INSTRUMENTAL ANALYSIS)

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2014

UNIVERSITI MALAYA

ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: **YEE CHUNG LEE**

I.C/Passport No: **881020-56-6419**

Registration/Matric No: **SGC 120004**

Name of Degree: **MASTER OF SCIENCE (ANALYTICAL CHEMISTRY & INSTRUMENTAL ANALYSIS)**

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

"ANALYSIS OF SELECTED LEAD-FREE SOLDERS BY OPTICAL EMISSION SPECTROSCOPY"

Field of Study:

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this Work,
(2) This Work is original,
(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work,
(4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work,
(5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained,
(6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

(Candidate's Signature) Date:

Subscribed and solemnly declared before,

Witness's Signature: Date:

Name: **DR LOW KAH HIN**

Designation:

Abstract

Characteristic studies were carried out to analyze 5 different types of lead free solder alloy. The concentrations of Pb, Cu, Fe, Ag and Ni in selected lead-free solders were determined by spark emission spectrometry and ICP-OES while their wettability were demonstrated by wetting balance. The Pb content found is well below the limit set in the Restriction of Hazardous Substances (0.1%). Subsequent statistical analysis revealed that there are five distinctive clusters of solders corresponding to their elemental contents, where the concentrations of Cu, Ag and Ni are the main discriminants.

Abstrak

Kajian ciri-ciri telah dijalankan untuk menganalisis 5 jenis aloi pateri bebas daripada plumbum. Kajian ciri telah dijalankan untuk menganalisis 5 jenis plumbum aloi pateri percuma. Kepekatan Pb, Cu, Fe, Ag dan Ni dalam solders bebas plumbum terpilih ditentukan oleh Percikan Pelepasan spektrometri dan ICP-OES manakala kebolehbasahan ditentukan oleh pengimbangan pembasahan. Kandungan Pb didapati adalah di bawah had yang ditetapkan dalam Sekatan Bahan Berbahaya (0.1%). Analisis statistik berikutnya mendedahkan bahawa terdapat lima kelompok tersendiri aloi pateri yang sepadan dengan kandungan unsur mereka, di mana kepekatan Cu, Ag dan Ni adalah discriminants utama.

Acknowledgements

First of all, I would like to express my deepest gratefulness to my supervisor, Dr. Low Kah Hin, for his guidance and supervision as well as patience throughout the course of my research. Without his valuable and comments suggestions, this project would not have been possible. Secondly, I would also like to acknowledge RedRingSolder (M) Sdn Bhd for sponsoring my study. In addition, I would also like to thank my colleagues and superior who give their advice, suggestion and help during my lab work. Lastly, I wish to thanks to my family members and my friends as well for their moral and financial supports.

Table of contents

List of Figures

List of Tables

List of Symbols & Abbreviations

American Society for Testing and Material	ASTM
Analytical Reagent	AR
Bismuth	Bi
Cadmium	Cd
Certified Reference Material	CRM
Charge-Coupled Device	CCD
Compact Disc	CD
Computerized Tomography scan	CT scan
Copper	Cu
Deionized	DI
Europe	Eu
Global Positioning System	GPS
Hydrochloric acid	HCl
Indium	In
Inductively Coupled Plasma	ICP
Inductively Coupled Plasma-Optical Emission Spectrometry	ICP-OES
Information Technology	IT
Integrated Circuit	IC
Japan Electronics and Information Technology Industries Association	JEITA
Lead	Pb
Microelectromechanical devices	MEMS

National Electronics Manufacturing Initiative	NEMI
Nickel	Ni
Nitric acid	HNO_3
Phosphorus	P
Photo-Multiplier-Tube	PMT
Printed Circuit Board	PCB
Restriction of Hazardous Substances Directive	RoHS
Silver	Ag
Surface-Mount Technology	SMT
Tin	Sn
United Kingdom	UK
United States Of America	USA
Waste Electrical and Electronic Equipment	WEEE
Zinc	Zn

List of Appendices

CHAPTER 1

INTRODUCTION

1.1 Definition of solder

Solder is a metal alloy which used to join the metal work piece(s) together in electronic applications, automotive components and plumbing products. In order to success the soldering process and enhance the quality of soldering process or the welding process, the solder that chosen for a particular soldering process must has lower melting point compared to the metal work pieces that going to solder (Solder, 2013). In electronics field, solder is an important and critical material to hold the electronic components together while allows them to transmit electrical signals to dissipate heat and allow other components to expand and contact. Various shapes and alloy compositions which each of them have its own unique properties, characteristics and function are available for solder product (Eric Bastow, 2005). Basically, solder is classified into two categories which are i) soft solder and ii) hard solder.

International Organization for Standardization (ISO) standard defines soft solder as "A metallic filler material which is used to join metallic parts and which has a melting temperature (liquidus) lower than that of the parts to be joined and, usually, lower than $450^{O}C$ and which wets the parent metals" (Soft Soldering Handbook, 2001). This means that soft solder is used in soft soldering to contact with the base metal surfaces and fill into the gaps between joint to form a new surface alloy by capillary action. The solder joint that done by soft soldering process can be very strong if the soldering process is done perfectly and the solder joint is made correctly. Since tin is the major contents of soft solder, therefore it is regarded as tin based solder as well. In order to enhance the soldering

performance of tin based solder, various types solder alloys composition have been introduced with the diverse composition of other metal elements such as lead (Pb), silver (Ag), copper (Cu), antimony (Sb), bismuth (Bi), nickel (Ni), indium (In), zinc (Zn) since tin has a good affinity to dissolve and join with these metals. (Solder Types and Uses the Categories and Correct Choice, 2009). In electronic devices assembly application, solder is normally used to bond two or more metallic surface and will melt below 350 ^{O}C. For instance, the combination usage of soldering gun (Figure 1.1) and soft solder (e.g. solder wire) which produced by mixture of tin and other elements are mainly to touch up the soldering joint on printed circuit board (PCB) in electronic line (Soft Soldering Handbook, 2001). Besides electronics application, soft solder also can be used to create custom base-metal jewelry, fuse base-metal components, repair costume jewelry, and solder shut base-metal jump rings (Soft Soldering Handbook, 2001).

Figure 1.1: Soldering iron

On the other hand, hard solder (or braze material) is metal alloy which the melting point is above 450 ^{O}C where this temperature is just slightly lower than the metal pieces to

be soldered and fused together by melting two or more parts and flowing filler metal into the joints by capillary action. Hard solder normally applied in brazing process (hard soldering) which generally requires a touch that offers considerably higher working temperature. In turn, titanium, aluminum, and stainless steel can be fused with hard solders. For example, silver hard solder is used in silver jewelry assembling by melting and flowing silver solder into the joint to join the parts together. It can also be adopted to fuse the brass or copper, however, the joints are different in color if silver hard solders are applied in the brass and copper assemble (Solder Types and Uses the Categories and Correct Choice, 2009). In the welding process, oxy-propane or oxy-acetylene flames are normally used to deal with hard solder, but butane flame also can be used for some soldering tasks such as solder the jump rings, create ball-end head pins, make custom wire links and chain, create small bezels, and fuse small metal components together (Soldering 101, 2013).

Based on the above mention classification analogy, there might be some ambiguous cases particularly when the melting point of a hard solder is low. That the reason why hard solder is further categorized into “easy”, “medium” and “hard” grades. In order to create a complex metal piece, it should start with hard solder, then fuse the next elements with medium grade hard solder then the easy grade hard solder is added at the last step. By using this way, the solder will hold the first elements tightly and will not flow or move while subsequent parts are added and assembled. "Chip", pallion or chippable forms are the most efficient ways of usage of these solders.

To sum up, soldering process is different from welding process where welding involving the melting of the metal work piece while that soldering does not melt the metal work piece (due to the lower melting point of solder than the metal work piece). Meanwhile, Soldering is distinguished from brazing by use of a lower melting-temperature

filler metal in soldering process while higher melting temperature of filler metal in brazing (Solder alloys, 2009).

1.2 History of Solder

Soldering is an ancient technique. Usage and the application of solder can be traced back to about 5,000 years in Mesopotamia (Joe, 2011). Many different soldering techniques were widely used in the Greek and Roman Empires, as well as in Viking dominated Scandinavia. Archeologists found that jewelry, weapons, tools, and cutlery were skillfully soldered in those Empires. For instance, eutectic tin-lead solder which able to present in both liquid and solid phases at a temperature point has been applied in electronics industry for more than six decades. This kind of solder is preferred by users because it able to applied with many lower melting point interconnection materials (Joe, 2011).

In past, hand labor and manual assembly were used in electronics assembly industry. Due to the low productivity of solder-based assembly under such circumstance, the assembly technology was then transitioned to automation for mass solder assembly. By changing of through-hole automated component assembly and soldering process to surface mount technology, the assembly productivity was gained significantly (Joe, 2011).

1.3 Soldering process

Soldering process is most frequently applied in assembling of electronic components on PCBs. Another common application is making permanent but reversible connections between copper pipes in plumbing systems. Joints in sheet metal objects such as food cans, roof flashing, rain gutters and automobile radiators have also historically been soldered, and occasionally still are. Jewelry components are assembled and repaired by soldering. Small mechanical parts are often soldered as well. Soldering is also used to join lead came and copper foil in stained glass work. Soldering can also be used to affect a

semi-permanent patch for a leak in a container cooking vessel (Soldering and Brazing, 2008)

In general, soldering is a mechanism where heat is applied to join two or more metal substances together. It is done by melting and flowing solder into the joint between the metal substances by capillary action and bonding materials to be joined by wetting action. The resulting joints are not as strong as the base metal, but they do have adequate strength, electrical conductivity, and water-tightness for various purposes. In other words, soldering is a method that used to make a permanent electrical and mechanical connection between metals, where the solder reacts with other metals chemically in order to form a different alloy. The elements that needed in soldering process are base metals, flux, solder, and heat (Mark and Barry, 1997).

Solder is one of the critical materials in soldering process. It is important to keep the solder that applied on soldering process free from impurities so as to produce strong solder alloy. This is due to the presence of other metals even tough in small quantity also might cause dramatic change in the surface tension. This will cause poor wetting which leads to poor solder joint; likewise the non-metal impurities such as dust, oil, vapors will weaken the solder bonds (Mark and Barry, 1997). Therefore, adequate control processes are required in soldering to prevent contaminant from electronic components entering the solder pot.

Base metal is the metal that contacts with solder and forms an intermediate alloy with solder. For example, if electronic components are attached to a PCB, the leads or the pins of the components and the board's metallic circuitry are the base metals. Copper, bronze, silver, brass, and steels-base metals are readily solderable; whereas high alloy steels, cast iron, and titanium are difficult or impossible to be soldered. For that reason, these materials are found in soldering machinery and act as temporary covers for

components that are not to be soldered in some cases (Mark and Barry, 1997). For example, since ceramic do not react with solder, which allows ceramic circuit board to draw liquid solder on it. In addition, the level of surface oxidation on a base metal is inversely proportional to reactivity of solder on that particular base metal. This means the more oxidation process, the more metal oxide on the surface, the weaker the solder bond (Mark and Barry, 1997). In fact, most metals are oxidizing at accelerated rate when they are heated due to the high temperatures during soldering process.

To overcome such problems, flux can be applied before soldering process to clean and to remove the metal oxide surface of base metals. (Mark and Barry, 1997). Basically flux can be divided into two basic parts, the chemicals and the solvents. The chemical portion includes the active components; while solvent is act as carrying medium. The removal of the residues of a flux is greatly depends on the solvent involved. Some fluxes can be removed with simple water treatments, while others require cleaning agents such as organic solvents, alcohol, and terpenes. Owing to their own characteristics, fluxes have numerous useful functions on soldering process (Mark and Barry, 1997).

Besides the oxide removal by its acidic nature, the flux that shielding the base metal from air can help minimizing the potential oxidation resulted from the elevated heating during soldering process. It is generally agreed that the stronger acid component in a flux, the greater the oxide removal power, yet this might continue to corrode the solder joints. This definitely will degrade the long term reliability of the assembly, if the flux residues are not being completely cleaned off or removed after soldering process (Mark and Barry, 1997).

1.4 Shape of solder products

Solder is typically transported and sold in solid form. Common forms of solder include anode (ball, button, pellet), bars, solder wire (with a core of flux), solid wire, and paste form. Each of which has advantages in different soldering processes. For example, reflow soldering requires solder paste to complete.

Solder paste is a substance with a cream-like consistency made up of solder powder, chemical flux, and additives which act as carrier. Putting the flux and solder together in the mixture has an obvious advantage when it comes to applying the substance to the base metals. It also presents a problem as highly corrosive flux cannot be used. This is due to the flux by nature is acidic and corrosive to the metal solder, which means that solder paste is inherently unstable. In general, the shelf life of a solder paste is about six months. The time between when the solder paste is applied to the base metal and completion of final heating is limited to a maximum of a few hours (Mark and Barry, 1997). Picture of solder paste is showed in Figure 1.2.

Figure 1.2: Solder paste

Besides, solder anode which including ball, button and pellet shape is suitable for electroplating process. This is because they have larger surface area over volume ratio as electroplating process requires fast action where the solder (mainly tin) can be deposited to the electrodes. The solder anode that used in the production site is not just based on the dimension of the bucket that used but also the solder consumption and oxidation rates (which depend on the buffer solution that used in the electroplating process). Although solder with various compositions have been introduced to improve soldering process, only pure tin is used in electroplating. Figure 1.3 shows various solder anodes.

Figure 1.3: Solder Anode

In addition, solder bar and solid wire are mainly used for wave soldering and dipping soldering process. Usually, such solder are used in the production line of semiconductor assembler where they are fed into the melting pot automatically. Therefore, the dimension and the weight of the solder bar and/or the solid wire are dependent on the design of the auto-feeder. Figure 1.4 shows the photo of solder bar and; Figure 1.5 is the

picture of solid wire with auto-feeder. In the case of hand soldering, solder wire that with a core of flux is basically used to the touch up the solder joints in the PCB. Figure 1.6 showing solder wire that normally used in touch up hand soldering method.

Figure 1.4: Solder Bar

Figure 1.5: Solid wire with auto-feeder machine

Figure 1.6: Solder Wire

1.5 Objectives of study

The objectives of this study are to evaluate and to compare the analytical performance of ICP-OES technique with Spark Emission Spectrometer in the determination alloy composition of solder especially those solder alloy which contains high amount of Ni, Cu and Ag and monitor the wettability of selected type of alloy composition.

CHAPTER 2

LITERATURE REVIEW

2.1 Leaded and Lead free solder

A solder is called as “leaded solder” if its major component is lead or contains high percentage of lead. Due to good characteristics such as low melting point, high flow rate, leaded solder was used over decades in electronics assembly. On the other hand, “lead free solder” do not contain a significant amount of lead (<0.1%)

On July 1, 2006 the European Union Waste Electrical and Electronic Equipment Directive (WEEE) and Restriction of Hazardous Substances Directive (RoHS) came into effect prohibiting the intentional addition of lead to most consumer electronics produced in the Europe (EU) or products that export to EU as California and China have their own version of RoHS. Implementation of RoHS is to reduce pollution caused by disposed electronic devices such as televisions, radios, games and other products In case of landfills, the hazardous lead from solders can be leached into municipal water supplies (Solder Alloys, 2009). Following table (Table 2.1) displays the maximum allowance in electronic devices listed under RoHS (2006) (RoHS regulation, 2011)

Table 2.1: Maximum allowance in electronic devices listed under RoHS

Lead, 0.1%max
Cadmium, 0.01%max
Mercury, 0.1%
Chromium VI, 0.1%max
PBB, 0.1% max
PBDE, 0.1% max

These include home appliance such as microwave oven, iron, refrigerator; neon lamp; Information Technology (IT) devices such as hand phone and computer; any consumer electronic devices such as television, camera; toys which have electronic function such as sound or light; monitoring devices such as weighing balance; some medical devices such as electronic thermometer. However, there are some exempted devices such as military devices; medical devices such as Computerized Tomography scan (CT scan) and ultrasound; automotive electronic devices such as radio, Compact Disc (CD) player and Global Positioning System (GPS); signal and transmission devices in telecommunication network.

Since lead element is restricted under RoHS, therefore, electronics or semiconductor relevant companies including solder manufacturers have switched to lead free product. Switching from leaded solder to lead free solder is a challenging mission due to appearance of some issues (RoHS Regulation, 2011). The main issue is the undesired tin whiskering as noticed in lead free solder. Besides that, the flow rate and the wettability of lead free solder is generally not as good as leaded solder, and the melting temperature is also higher than leaded solder. These issues have brought about some associated concerns likes more energy

is needed to melt the solder in the production, solderability and etc. However, the flow rate and the wettability problems in lead free solder could be solved by forming solder alloy with different elements such as copper and silver.

Two reliability problems may encountered from the tin whiskerings. First is electrical shorting, as the whiskers grown between adjacent conductors of different potentials. This can cause transient short if the whisker is burned open, or a permanent short. Second are the potential mechanical problems with slip rings, optical devices, microelectromechanical devices (MEMS) and other similar components. In another context, higher melting point means that the melting pot must able to sustain high temperature so as to prevent dissolution. In fact most of lead-free solder replacements have melting points from 5–20 ℃ higher than the conventional leaded solder, e.g. Sn60/Pb40 and Sn63/Pb37 (Puttlitz and Stalter, 2004). Higher melting points and decreased flow rates causing longer contact period required in joining a lead-free solder with the connections. In order to compensate these negative effects of lead-free solder, various alloys have been invented with wide range tin-metals composition.

In response to the new wave of regulations, there are several desirable attributes has been compiled for lead free solder. Table 2.2 below shows the attributes or requirements in lead free solder alloy selection.

Table 2.2: Attributes or requirements in lead free solder alloy selection.

The selected element will have no negative environmental impact now or in the future
Sufficient quantities of base materials must be available now and in the future
Melting temperatures similar to 63/37 tin/lead, preferably below 200 ℃
Equal or similar thermal and electrical conductivity
Adequate joint strength and thermal fatigue resistance
Easy repairability
Low cost
Compatibility with existing processes.

(Solder alloys, 2009)

2.2 Different types of solder alloy composition

2.2.1 Pure tin

Tin is used in several industries such as food industry, plating industry and electrical and electronic industry. In electrical and electronic industry, tin is used to produce pure tin solder (Sn> 99.9%) with the melting point of 232 ^{O}C or as base material to produce other types of alloy. Ogot, and Kremer (2004) claimed that the features of pure tin solder are good strength, non-dulling. Pure tin solder alloy mainly used in electroplating soldering technique. However, it is susceptible to tin pest (Ogot and Kremer, 2004).

The advantages of pure tin solder alloy are simple and cost effective. Meanwhile, the disadvantages are electrical shorting and potential mechanical problems which caused by the tin whisker and tin pest (Carabello, 1998).

2.2.2 Tin- Copper

The ordinary composition of this solder alloy that being used widely is Sn99.3Cu0.7 with melting point of 227 ^{O}C. This alloy composition is cheaper alternative for wave soldering, which is recommended by the US National Electronics Manufacturing Initiative (NEMI) consortium. However, its high melting point unfavorable for Surface-Mount Technology (SMT) use. The main features of this alloy are low strength, and high ductility. Similar to others lead free solder, tin-copper solder alloy is susceptible to tin pest.

The advantages of this alloy are lower cost, dissolves less copper in coating process, more stable intermetallic layer, and less attack on Solder Pot. The disadvantage is higher melting point if compared to tin-silver alloy or tin-silver-copper alloy, therefore higher temperature, and more heat is generated in the soldering process. Besides that, tin-copper solder alloy may not suitable for all type of wave soldering due to its liquidus and density. Yet, addition of trace amount of nickel into the molten solder able to increases its fluidity, the highest increment is at 0.06% of nickel. Such nickel modified or nickel stabilized tin-copper solder which suitable for Wave Soldering and Hot Air Leveling (Karl J. Puttlitz, and Kathleen A. Stalter, 2004). In addition, tin copper solder alloy has claimed to be poor wettability and low thermal resistance (Carabello, 1998).

2.2.3 Tin-Silver

The commonly used tin-silver solder alloy composition is Sn (97%) Ag (3%). The melting point of this composition of solder alloy is 214 ^{O}C. Tin-silver solder alloy is commonly used in wave soldering and reflow soldering technique.

2.2.4 Tin-Silver-Copper

There are many composition types for such solder alloy. The commonly used composition is Sn (96.5%) Ag (3.0%) Cu (0.5%) with melting point of 220 ^{O}C. Tin-copper-silver solder alloy, especially Sn (96.5%) Ag (3.0%) Cu (0.5%) is recommended by Japan Electronics and Information Technology Industries Association (JEITA) standard for wave and reflow soldering. Besides wave and reflow soldering, this solder alloy composition also usable also for selective soldering and dip soldering. The widespread use of this popular lead-free solder alloy family is based on the reduced melting point of the Sn-Ag-Cu ternary eutectic behavior (217 ^{O}C), which is below the Sn-3.5Ag (wt%) eutectic of 221 ℃ and the Sn-0.7Cu eutectic of 227 ℃. It is important to maintain low molten solder bath temperature because high temperature causes detrimental effect such as increasing of bridging due to copper buildup. Besides that, in order to maintain the fluidity and the melting point of the alloy in the molten solder bath, copper content must be maintained between 0.4–0.85 %. This level can be maintained by refilling the molten solder bath with Sn97Ag3 alloy. In some cases, nitrogen atmosphere can be used to reduce losses by dross formation (Yun Zhang, 2010).

To sum up, the advantages of tin-copper-silver are high reliability, good solderability, and greater ability to cope with lead contamination. Meanwhile, the disadvantages are higher melting temperature, higher cost due to high silver content, possibility of micro-cracking, and patent issues, particularly outside Europe (Yun Zhang, 2010).

3.4 Function of Metal Elements in Alloy Composition of Lead Free Solder

As demonstrated in previous section, different types of solder alloy show different characteristics and different properties. This reflected that the element composition plays crucial roles in the solder alloy. Each element introduced can well be associated with the solder's physical and chemical properties as well as their characteristics.

2.3.1 Silver

In general, silver provides mechanical strength and fluidity to solder alloy. However, it has worse ductility if compare to lead. In lead free solder alloy incorporation of silver elements might improves resistance to fatigue from thermal cycles. (Solder Alloys, 2009).

2.3.2 Copper

Copper shows the characteristic of lowering the melting point of solder alloy. Besides, it also improves the resistance to thermal cycle fatigue, and improves wetting of solder. In addition, it slows down the copper dissolution rate from board and part of lead of components into molten solder (Solder Alloys, 2009).

2.3.3 Zinc

Zinc has the ability to lower the melting point and it is cheap in term of cost. However it is easily being corroded and oxidized in air. Therefore zinc-containing alloys or the molten solder which contaminated by zinc are not suitable for some soldering technique, such as wave soldering. This is because of the high amount of zinc (>0.003%) may causes bridging and icicling and higher surface oxidation in solder bath. (Solder Alloys, 2009).

2.3.4 Iron

High iron contents cause gritty joint formation and bridging which due to $FeSn^2$ intermetallic compound needles. High iron in solder bath most probably indicates pot erosion and leakage of iron from melting pot. This is due to corrosion of the iron melting pot by lead free solder.

2.3.5 Phosphorus

The function of the introduction of phosphorus is to reduce dross by preventing oxidation of the surface of molten solder. This is because dross might reduce the wetting properties and solderability of the surface of molten solder. Xian and Gong (2007) demonstrated that addition of trace amount of phosphorus able to reduce the oxidation process and hence reduce the dross formation optimally. Figure 2.1 indicates that the oxidation rate is reduced from 2.8×10^{-4} mg mm^{-2} min^{-1} to 1.0×10^{-4} mg mm^{-2} min^{-1} when the phosphorus concentration in solder is increased from 42 ppm to 56 ppm.

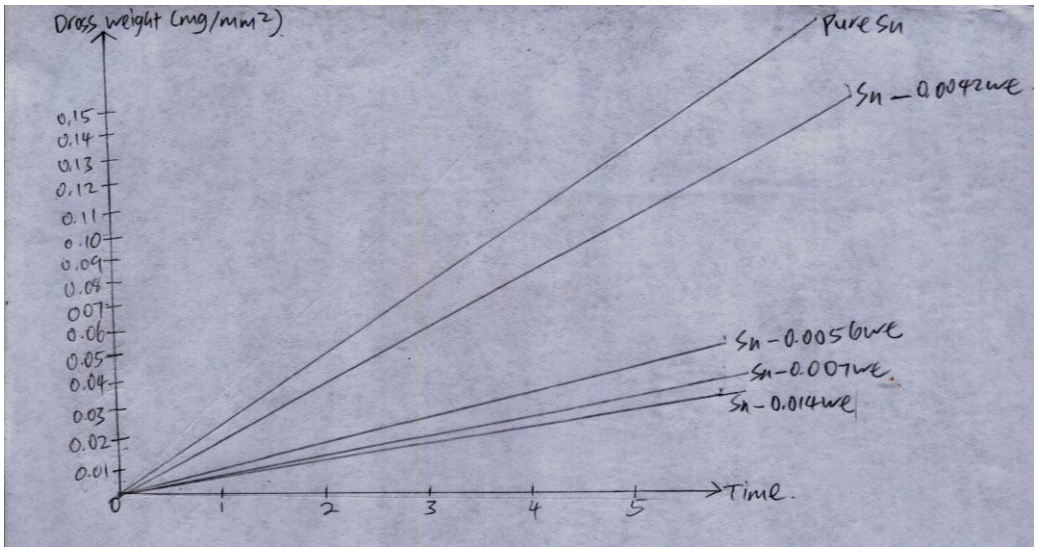

Figure 2.1: The relationship between the accumulative dross weight on the surface and the oxidation time at 280^{O}C (dross removal at 1 hour intervals) (Xian and Gong, 2007).

2.3.6 Nickel

Nickel acts as barrier in soldering process by minimizing the dissolution of copper therefore retards the excess growth of Cu-Sn intermetallic compounds. This is because nickel able to prevent rapid reaction between the solder and the copper layer of PCB. Copper preservation is important when the circuit features continue to shrink and signal integrity become as critical issue. (Solder Alloy, 2009) However, if the nickel contents are higher than 0.025%, it will slow the wetting speed and affect the hole fill performance due to the liquidity of the molten solder being decreased by nickel.

The availability and the amount of different elements may affect the physical and chemical properties of the solder which further the wettability of the solder which highly dependent on the temperature and fluidity of the molten solder.

2.4 Wettability

Wetting is defined as the ability of the molten solders to flow or spread on a metal surface. Is an important characteristic which accounts the strength of metallurgical bond formed in soldering system and particularly and essential consideration in electronics assembly (Duong *et al.*, 2008).

In order to quantitatively evaluate the wettability in soldering process, the contact angle and the interfacial tension should be first considered. In this context, the degree of wetting can be defined by the value of the contact angle, θ. There are a few common degree of wetting (Takao *et al.*, 2004.).

1. Fully Wet ($\theta = 0$)

This degree of wetting indicates the optimum condition where complete wetting occurred and perfect metallurgical bond has formed.

2. Non wet ($\theta = 90$)

Non-wetting is the condition in where metallurgical bond is not formed.

3. Partially Wet ($0° < \theta \leq 90°$)

Partial wetting is defined solely on the basis of visual observation, in the case where metallurgical bond has formed, but the contact angle is larger than zero.

4. De-Wetting

In this degree of wetting, the substrate appears to be wet fully initially. After a period of time, the molten solder begins to recede, exposing substrate area which had initially been covered by molten solder. De-wetting is usually caused by extensive growth of an intermetallic or an impurity inclusion (Romig *et al.*, 1991).

There are many techniques can be used to measure the degrees of wetting such as Parallel Plates, Sessile Drop, Dip Test, and wetting balance (Romig et al., 1991). Among them, wetting balance is one of the most commonly used. In this method, a specimen that suspended from a sensitive balance is immersed into the studied molten solder bath at a constant temperature with a controlled rate and is wetted (Figure 2.2). The force that implied on that specimen, while immersed, is measured. Indices of wettability, such as wetting time and wetting force (opposing vertical force of buoyancy), and surface tension can be subsequently extracted by taking the buoyancy into account. The results highly depend on the substrate size and shape because the wetting curve depends on the heat capacity. Besides that, the results are also affected by the fluxes that applied on the specimen (Takao *et al.*, 2004).

For use with surface mount components, some modifications may be required. The specimen is first fluxed and hung on the balance over the solder bath for a predetermined time such that it is effectively preheated by convection from the solder. The specimen is then immersed, usually at a speed of 15 mm s^{-1}, to a predetermined depth and held in that position for a specified time (usually about10 - 20 s), before withdrawal. The force experienced by the specimen as a function of time is recorded. Figure 2.2 shows a typical six stages of the testing of a specimen that is readily wet by the solder. In this curves, the two important parameters can be extracted as wettability indices are wetting time and maximum wetting force (Fmax). The wetting time is the time for the meniscus to pass through a contact angle, θ=90^{O}, or for the measured wetting force to decrease to zero, point 9(c). The Fmax corresponds constant force when the meniscus stabilized after immersion, point (d) (Duong *et al*., 2008).

Figure 2.3 shows some representative curves. In each case, the full horizontal line represents the force condition at the start of the test cycle and the dotted horizontal line represents the buoyancy level at which the wetting force is zero (the contact angle is 90^{O}")(Romig *et al*., 1991). The buoyancy of the specimen is simply the product of the immersed volume (measured from the mean liquid level, not from the meniscus level) and the density of the solder. One of the main advantages of the wetting balance technique is the ability to monitor and record explicitly wetting force as a function of time (Romig *et al*., 1991). Poor wetting of the base metals will lead to poor solder joint The three conditions which causing poor solderability are excessive thickness of the intermetallic layer, excessive amounts of oxides and other surface contaminants on the plating, and high levels of codeposited carbon from the organic brighteners in bright tin coatings (Mark and Barry, 1997).

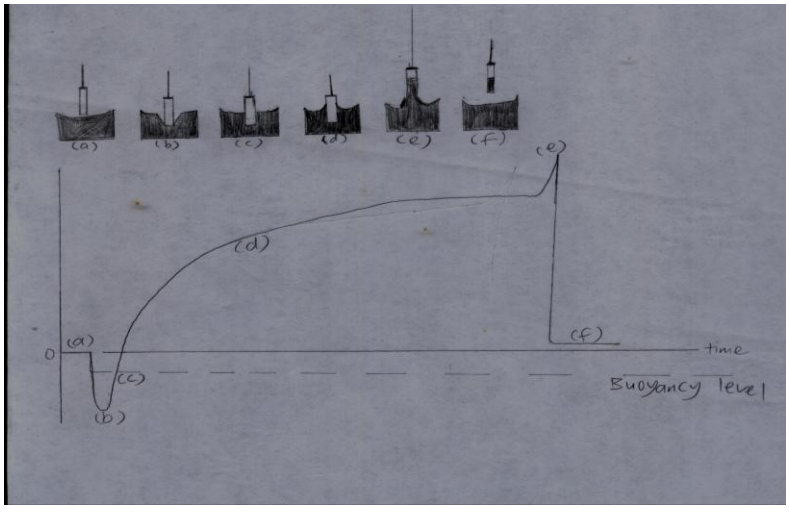

Figure 2.2: Six stages of the testing of the specimen that is readily wet by solder (Romig *et al*., 1991)

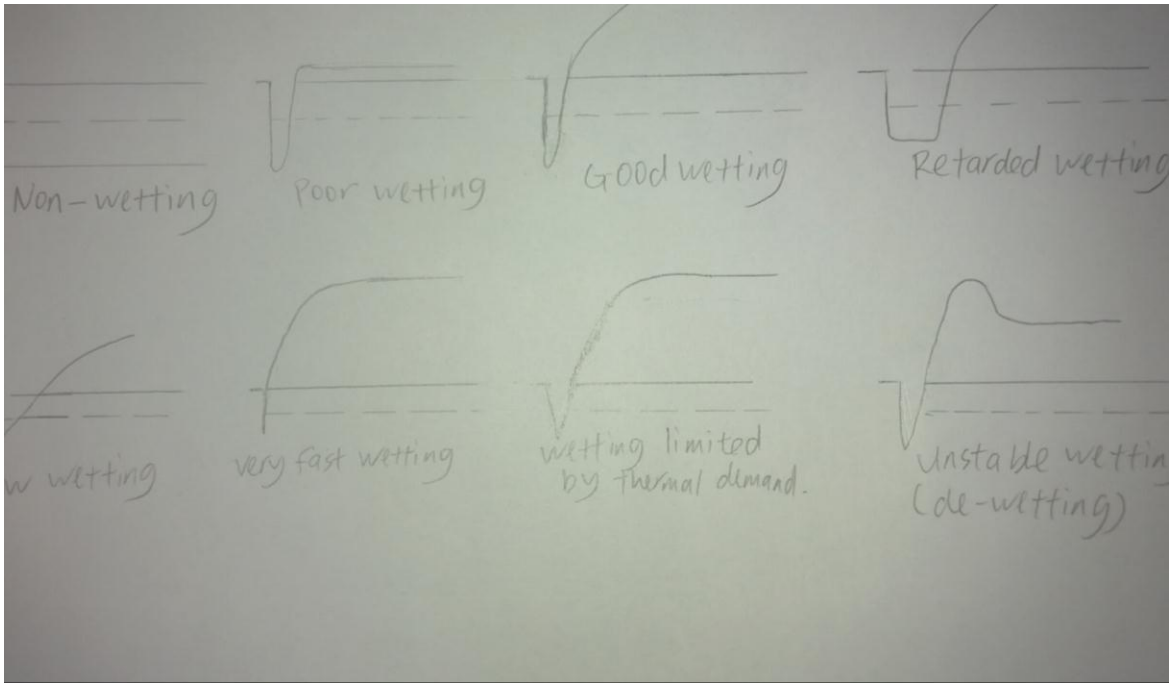

Figure 2.3: Representative shapes of w e t t i n g balance curves for different degree of wetting (Romig *et al*., 1991).

2.5 The Analysis of Solder Composition

Elemental analysis in solder is to ensure the alloy composition is within specification and to monitor the contamination in production process. Serious elemental contamination especially copper element might affect wettability of solder in soldering process. Elemental analysis can be done by atomic spectroscopic techniques such as Spark Emission Spectrometer and ICP-OES

2.5.1 Spark Emission Spectrometer

Spark atomic emission spectroscopy can be used on both conductive and non-conductive materials. Analysis of metallic elements in solid samples can be done directly, whereas non-conductive materials, can be ground with graphite powder to make it conductive (Optical Emission Spectroscopy, 1998). Since solder consists of conductive

metal alloy, therefore, the analysis can be done directly without any sample treatment and result can be obtain within a minute.

Spark Emission spectrometer is introduced and used in Quality Control (QC) of daily production of solder due to usage convenience, fast analysis and high accuracy of the result in elemental analysis of varies solder alloy (Optical Emission Spectroscopy, 1998). These are important because production process is flow continuously and couldn't suspend and wait for few hours to get the analysis result before proceed to next step and there are plenty of samples in daily production.

Before analysis, solder sample is prepared by casting it into goblet and ensure the bottom surface which connect to counter electrode is flat. The prepared sample is placed on the bench of the instrument and the analysis system is flooded with argon. Prior actual measurements, the sample surface is subjected to high power discharges environment to melt so as to create a more homogeneous condition. High purity argon is used as discharge atmosphere in order to prevent any interaction between the atmospheric gaseous and the sample surface. An example of this set up is illustrated in Figure 2.4. Next, high energy sparks are created at gap between an electrode (cathode) and the prepared sample's surface (anode) which is argon-filled. The sparks that generated will ionize the argon, creating a conductive plasma to melt, evaporated, atomized and excite the solid sample. When the excited atoms relax to a lower energy state, they emit light at characteristic wavelengths. (Quantitative chemical analysis, 2010).

The photons of the interested element wavelengths are detected by Photo-Multiplier-Tubes (PMTs) or Charge-Coupled Device (CCD) detectors and transformed into electrical signals. The intensities of emissions are compared to intensities of standards to give quantitative results. All metallic elements (including carbon, sulphur, and phosphorus)

can be detected simultaneously in the parts-per-million range (Quantitative chemical analysis, 2010).

One of the advantages of spark emission spectrometry is it enable direct elemental analysis of pure metals and metal alloys. Besides, spark emission analysis is extremely fast and analysis result of plenty elements (up to 40) in metallic samples could be obtained within a minute.

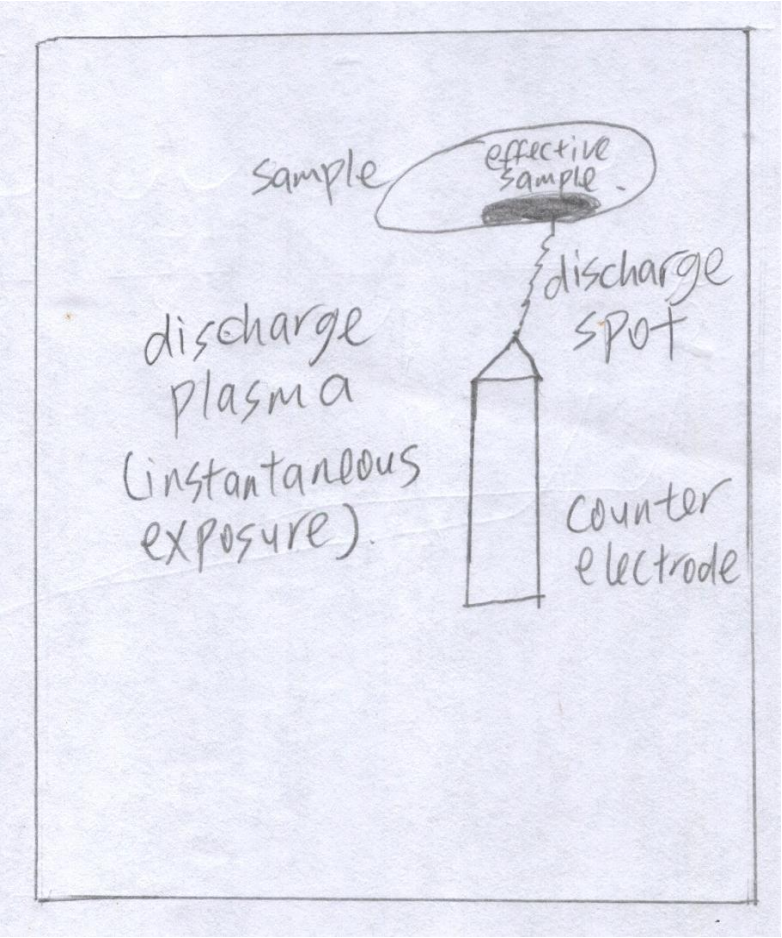

Figure 2.4: Sample excitation by electrical discharge (Optical Emission Spectroscopy, 1998)

2.5.2 **Inductively Coupled Plasma**

ICP-OES is commonly used to measure trace elements in samples qualitatively and quantitatively. It has the characteristics of high sensitivity, high reliability, wide dynamic range, and relatively less affected by spectra interferences. ICP-OES application is wide, such as purity analysis of environmental water, food elemental analysis and composition & impurities analysis of organics and inorganics as metals, ceramics, and plastics. Figure 2.5 is Perkin Elmer ICP-OES 8000 (Yosuke and Atsushi, 2008).

Figure 2.5: Perkin Elmer ICP-OES Optima 8000

ICP-OES is introduced in the solder because it give better sensitivity and the result is more representative because sample is drilled at different points and treated during sample preparation; (compared to sample is just sparked at a point if the analysis is done by Spark Emission Spectrometer). Besides, some elements at high concentration could not be quantified by Spark Emission Spectrometer due to lack of Certified Reference Material (CRM); while ICP-OES analysis is more dependent on sample preparation method, so the

concentration range is wider and is not limited by the availability and the concentration of CRM.

However, ICP-OES analysis requires a skilled scientist to operate the instrument and analyze the data. The instrument requires an advanced and elaborate laboratory facility to support the steps that involved in ICP analysis such as exhaustion to suck the toxic fumes generated during sample preparation, advanced water system to produce high quality water with low or no metal element, and proper waste disposing procedure. (Ismail and Yoo, 2010).

In some ICP instrumentation, there are two optical spectrometry view in ICP-OES which are axial view and radial view. Axial view is parallel view of the plasma; while radial view is view from the direction perpendicular to the plasma. Radial view is less affected by coexisting elements but has lower sensitivity, whereas axial view is greatly affected from coexisting elements but provides greater detection sensitivity, more than 10 times that of radial view for some elements.. Axial view and radial view of ICP-OES are shown in Figure 2.6 and figure 2.7 respectively (Yosuke and Atsushi, 2008).

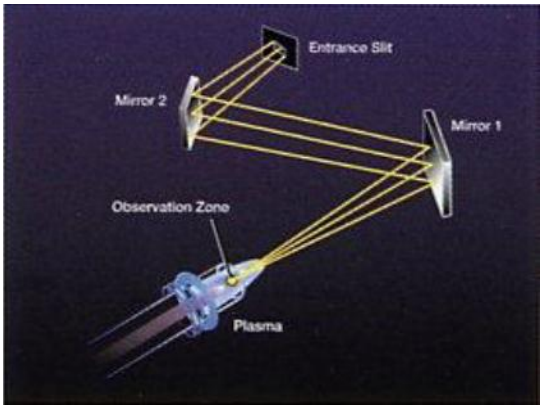

Figure 2.6: Axial view of ICP-OES (Yosuke and Atsushi, 2008)

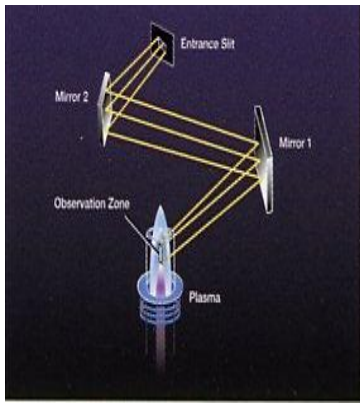

Figure 2.7: Radial view of ICP-OES (Yosuke and Atsushi, 2008)

ICP-OES is "gold standard" method to confirm RoHS compliance on Pb and Cd elements for many electronic components due to its sensitivity and accuracy. It is regarded as a key techniques measuring elemental content in a wide concentration range of variety of sample matrices by international standard organizations such as American Society for Testing and Materials (ASTM).

In ICP-OES analysis of solid samples, the samples are first to be dissolved in a solution. The solution is then nebulized into fine aerosols that passing through spray chamber to sort out big aerosols by depositing them on the wall of spray chamber. Only aerosols smaller than critical diameter able to be carried by plasma gas flow to injector and plasma torch. The aerosols are ionized in the plasma torch by spraying the sample solution into a high-temperature plasma (6000-8000K) which generated by subjecting argon gas to a high frequency field. This process produces atomic and ionic lines emission of interested elements of the samples. The concentration of analyte of sample solution is determined by comparing the intensity of emissions from the sample solution and the calibration solution (Yosuke and Atsushi, 2008).

The possible interferences in ICP-OES are nebulizer interferences, chemical interferences, ionization interferences and spectral interferences. First, nebulizer interferences (matrix effects) are physical and chemical differences between standards and

samples, such as the inconsistence presence of matrix salts and organic compounds or different viscosities and surface tension of the liquid. Next, chemical interferences are less common in ICP-OES due to high plasma temperature, long residence time of analytes in plasma, and inert atmosphere of the Ar plasma where the sample aerosols are completely burned in plasma. On the other hand, ionization interferences of ICP, usually affect the easily ionized elements such as alkali and alkaline earth elements. Last but not least, spectral interferences is possible in ICP analysis and it is common in high temperature plasmas as opposed to flame-based systems given the complete excitation and subsequent emission of all compounds in the sample (including the argon) (Dunnivant and Ginsbach, 2009).

CHAPTER 3

METHODOLOGY

3.1 Workflow diagram

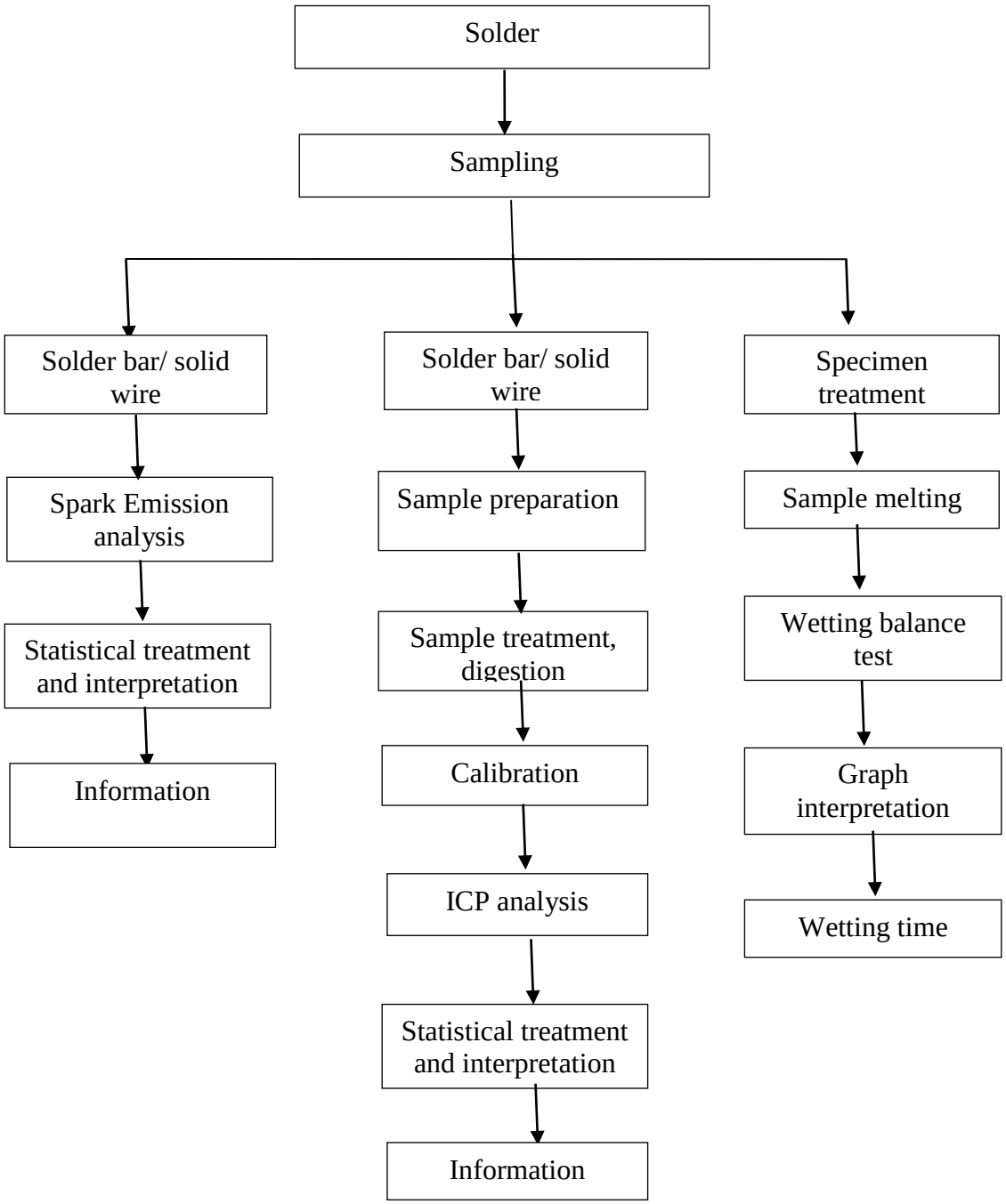

Figure 3.1: Workflow diagram of experiment.

3.2 Sample

Three individual lots of lead free tin based solder (either in bars form or wires form) with code number G220, G214, G227, G233 and G354 as shown in Table 3.1 were collected from the RedRingSolder's store.

Table 3.1: Solder samples and their lot number

Solder Code	Lot Number		
G220	1309654	1309657	1310732
G214	1305285	1310701	1310729
G227	1306415	1306449	1308618
G233	1310755	1310760	1310768
G354	1308587	1311793	1311818

3.3 Chemicals

Chemicals that listed in table 3.1 are used without further treatment unless it is stated.

Table 3.2: Chemical used in experiment

Chemical	Company
37% AR grade hydrochloric acid	Fisher Scientific (Malaysia)
65% AR grade nitric acid	Fisher Scientific (Malaysia)
1000 mg/L Phosphorus standard	Perkin Elmer (USA)
QC 21 standard (100 mg/L of Pb, Ni, Cu, Fe)	Perkin Elmer (USA)

QC 7A standard (50mg/L of Ag)	Perkin Elmer (USA)
Filter cartridge (C114) for DI water	ELGA (UK)
4MΩcm deionized water	Filtered and Purified by ELGA filter cadtridge

3.4 Spark Emission Spectrometer

3.4.1 Solder bar

Without any sample treatment, the bar was placed on the bench of Spark Emission Spectrometer and it was connected with the counter electrode which located at the bottom of the bench. Sample was analyzed by Spectro lab SpectroMaxX Spark Emission Spectrometer which using software of "Spectro Spark Analyzer Vision MX" with the part no. of 80011598. The steps above were repeated for the rest of samples.

3.4.2 Solid Wire

20 grams of solid wire were taken from store and melted at 250^{O}C. Molten solder is then casted into goblet shape with the diameter of 3cm by pouring the molten solder into a mould. The casted sample was analyzed with the procedure just mentioned for solder bar and repeated for the rests.

3.5 ICP-OES analysis

3.5.1 Calibration standard preparation

100 mg/L phosphorus standard solution was prepared by pipetting 5.0 $\pm$ 0.03 mL of 1000 mg/L into 50.0 $\pm$ 0.05ml volumetric flask. After that, 2.5mL of 37% AR grade HCl was added into the volumetric flask and marked up by deionized water. Then, a series of

external standard which contained Phosphorus, Lead, Iron, Nickel, Copper and Silver with the concentration of 0.01 ppm, 0.05 ppm, 0.1 ppm, 0.5 ppm and 1.0 ppm was prepared by appropriate dilution of 100 mg/L phosphorus standard solution, QC 21 stock standard solution and QC 7A stock standard solution.

3.5.2 Sample preparation and determination

3.5.2.1 Solder Bar

Both upper side and bottom side of a piece of solder bar was drilled and slices are kept in labeled plastic bag. After that 0.5 ± 0.1 g of solder sample was accurately weighted into a 100 mL beaker. 25 ml of 37% HCl was added and then heated at 220^{O}C for 1 hour. HCl was topped up in to the sample solution, if the volume is less than 20 ml. 10 drops of 65% AR grade HNO_3 were added into the solution mixture where there was black residue. The solution mixture became clear with light yellow after the addition of HNO_3. The sample was then heated for another 30-45 minutes. Heating process was controlled carefully in order to prevent the formation of white precipitate. Additional 5 drops of HNO_3 were introduced if the black sample particles still persist.

If there is white precipitation, 37% AR grade HCl was topped up to about 30 mL and heat at 220^{O}C so as to dissolve them. Before proceed to next step, the solution was ensured to be clear with no precipitate. When sample is fully dissolved, the solution mixture was further heated at 220^{O}C to evaporate the HCl until about 15 mL of the solution mixture is remained. The solution mixture was filtered into a 100 mL volumetric flask that had been filled with 10 mL HCl. The beaker was then rinsed by DI water for three times and the rinses were added to volumetric flask. Then, the filter paper was rinsed by DI water. The solution mixture was marked up by DI water. The resulting solution was shake gently to ensure its homogeneity. For a sequential dilution, 5 mL of HCl and 0.5 ± 0.002 ml

of the resulting sample solution were added into second volumetric flask. The solution mixture in the second volumetric flask and then marked up by DI water. Again, this was shaken gently before being analyzed with Perkin Elmer Optima 8000 ICP-OES which using software of "Perkin Elmer WinLab32 for ICP". The procedure was repeated the rest of solder bar samples.

3.5.2.2 Solid Wire

20 grams of a particular lot of a solid wire were melted at 250^{O}C. The molten solder is then casted into goblet shape with the diameter of 3cm. The casted sample was analyzed with ICP-OES using the procedure that applied on solder bar and these were repeated for the rest of solid wire samples.

3.6 Wettability test

3.6.1 Preparation of specimen

3.6.1.1 Copper coupon

Copper plate was cut into small pieces with the dimension of 1.2cm height and 0.9cm and 0.45 cm width. The copper plate is then ground and polished by using 800/640 grade sand paper to remove the oxide layer which coated on the surface of copper plate.

3.6.1.2 Leaded IC component

Leaded IC component was used directly without any treatment.

3.6.2 Solder loading and determination

800 grams of solder bar or solid wire sample were loaded into the melting pot of the wetting balance. The sample was melted and hold at 250 $\pm 3^{O}$C throughout the testing. The specimen was mounted and fixed on a holder before being immersed into the diluted flux at room temperature to a minimum depth of 5 mm. The excess flux was drained off immediately by standing the specimen vertically on a clean filter paper. After partial dried, it was mounted on the specimen holder of the Tarutin SWET 100 wetting balance. The surface of molten solder had been skimmed before analysis.

The specimen on the holder was held for 10 ± 1 seconds at the position 3mm above the solder pot initially. It was then dipped into the molten sample at an immersion and emersion rate of 20-25 mm per second to a depth of 5.0 ± 0.1 mm with a dwell time of 5.0 ± 0.5 seconds. The resulting wetting curve was recorded.

CHAPTER 4

RESULT & DISCUSSION

Table 4.1: LOD and LOQ of variable elemental analysis by ICP-OES

Element	LOD/ppm	LOQ/ppm
Pb	0.03	0.06
Ni	0.04	0.1
Fe	0.4	0.9
P	0.1	0.2
Cu	0.1	0.3
Ag	0.1	0.3

LOD: mean of blank + 3 standard deviation of blank
LOQ: mean of blank + 10 standard deviation of blank

Table 4.2: Wetting time of different solder alloy on copper coupon and IC component

Alloy code	Alloy composition	Wetting time for half copper	Wetting time for full copper	Wetting time for IC component
G220	Sn 96.5 Ag3.0 Cu0.5	0.95 sec	1.35 sec	0.47 sec
G214	Sn97 Ag3.0	1.1 sec	2.27 sec	0.45 sec
G354 (250^{O}C)	Sn96.0 Ag3.5 Ni0.475	1.1 sec	1.2 sec	0.65 sec
G354 (350^{O}C)	Sn96.0 Ag3.5 Ni0.475	0.35 sec	0.5 sec	0.15 sec
G227	Sn 99.3 C 0.7	1.65 sec	2.6 sec	0.55 sec
G233	Sn 99.9	1.97 sec	2.55 sec	0.6 sec

4.1 Hierarchical Cluster Analysis

Hierarchical cluster analysis (HCA) employing Ward's linkage was applied to the study of similarity of the solder samples on the basis of the distribution of Pb, Ni, Fe, Cu and Ag in the solder samples. Both the dendrograms represented in Figure 4.1 (based on the spark emission spectroscopy data) and Figure 4.2 (based on ICP-OES data) consistently suggested that high variation in the elemental composition of G220, G227, G214, G233 and G354 due to the formation of five distinctive clusters. In order to explore the elemental

variables that associated with the partitioned clusters, principal component analysis was carried out.

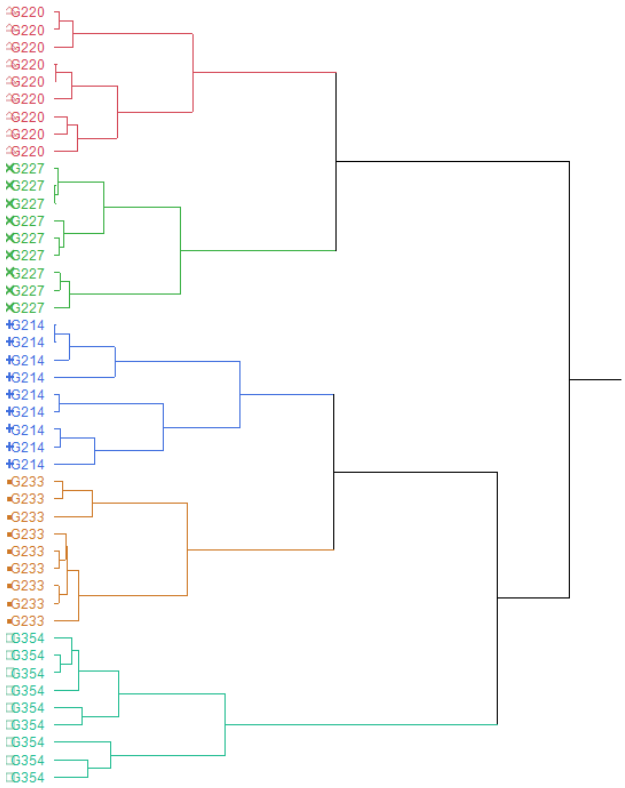

Figure 4.1 Dendrogram with Ward's linkage based on the multiple elemental data from spark emission spectroscopy

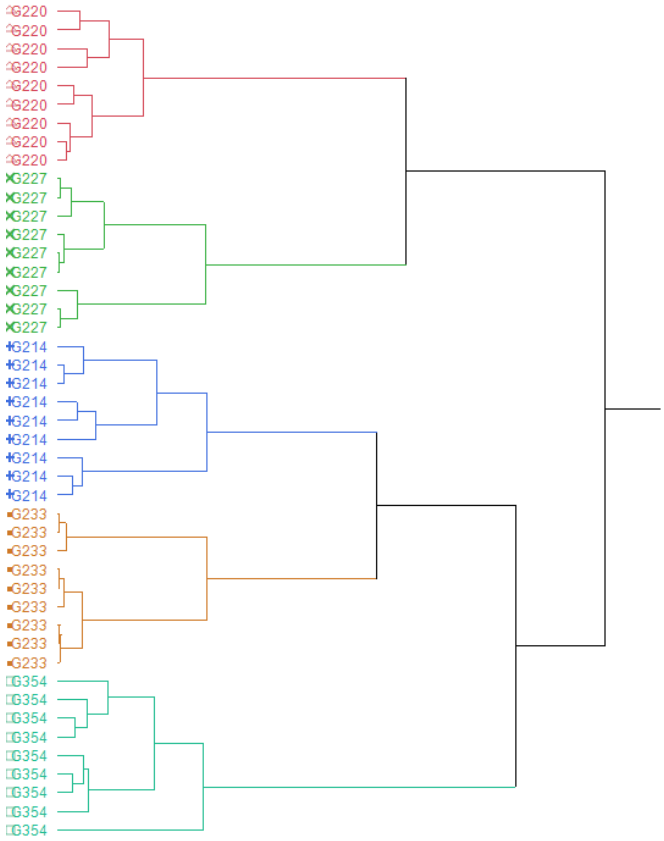

Figure 4.2 Dendrogram with Ward's linkage based on the multiple elemental data from ICP-OES

4.2 Principal Component Analysis

PCA allow matrices with multiple variables to be probed into a relative small number of dimensions by decomposition of the original data matrix into a product of scores and loadings matrices. This eases the perception of the multivariate nature of the data in the reduced dimensions. Figure 4.3 shows the bi-plot that maps both the loadings and the scores projected onto the first two principal components (PCs) in parallel, which accounted about 73% of total variance. This enables simultaneous interpretation of possible sample clusters and their corresponding elemental composition.

From Figure 4.3, it is noticed that the dispersion of the samples' scores along PC1 are mainly corresponding to their Cu, Ni and Fe composition, whereas PC2 is mainly

associated with Pb and Ag composition. For instance, solder samples coded with G220 and G227 that located on the negative region of PC1 are expected to be associated with higher Cu compositions compared to others; whereas G354 and G214 with positive PC1 scores can be characterized with Ni and/or Fe and/or Ag; while G233 are discriminated from the others with almost zero score on PC1 and negative scores on PC2. Likewise, five non-linear separated clusters that consistent with HCA finding are revealed. This reinforced that their elemental compositions vary considerably, and thus they might demonstrate different solderability.

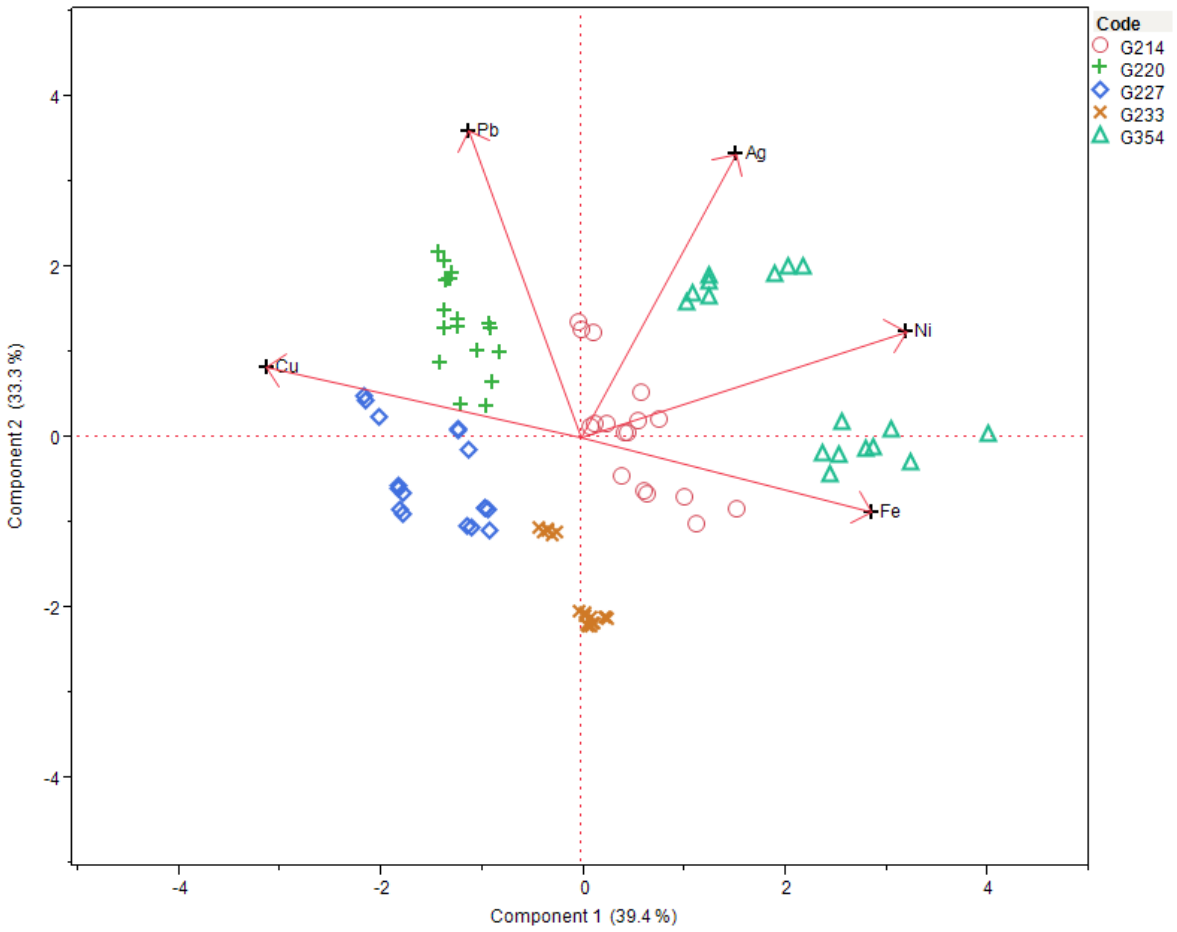

Figure 4.3 PCA bi-plot.

4.3 Univariate Statistical Analysis

In order to explore the link between elemental composition and the solder clusters in details, the analytical results were further evaluated. From the result, the observed lead concentration in the solder samples found to be $(1.9 \pm 0.2) \times 10^2$ ppm, which is significantly below the maximum allowance listed under RoHS (P<0.001). In details, Figure 4.4 shows that the Pb contents in the samples could be generally classified into 3 concentration ranges. The first level is the lowest Pb contents which contributed from G233 (pure tin solder). It is then follow by G214, G227 and G354; while G220 shows the highest Pb contents. Basically lead contents in solder alloy are mainly contributed from the raw material of tin. However, other raw materials such as copper, silver and nickel also contribute lead into the solder alloy.

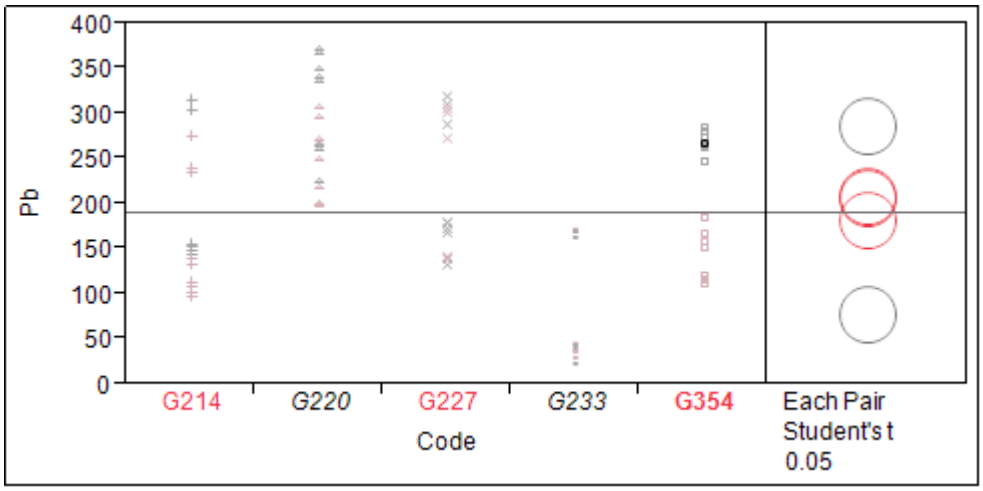

Figure 4.4: One way analysis of Pb content

Figure 4.5 shows the distribution pattern of Ni in the solder alloy. Obviously there are two distinct levels of Ni that could be present in the studied solder alloys. Samples coded with G354 found containing the highest concentration of Ni (0.42 ± 0.04) %, whereas Ni just present as impurities in others. This makes Ni a good variable for

distunguishing the G354 from the rests eventhough there are high variations in the measurement present as impurities. These variations are due to certain descrepancies within the sample lots, replicates and analytical methods which require further investigation.

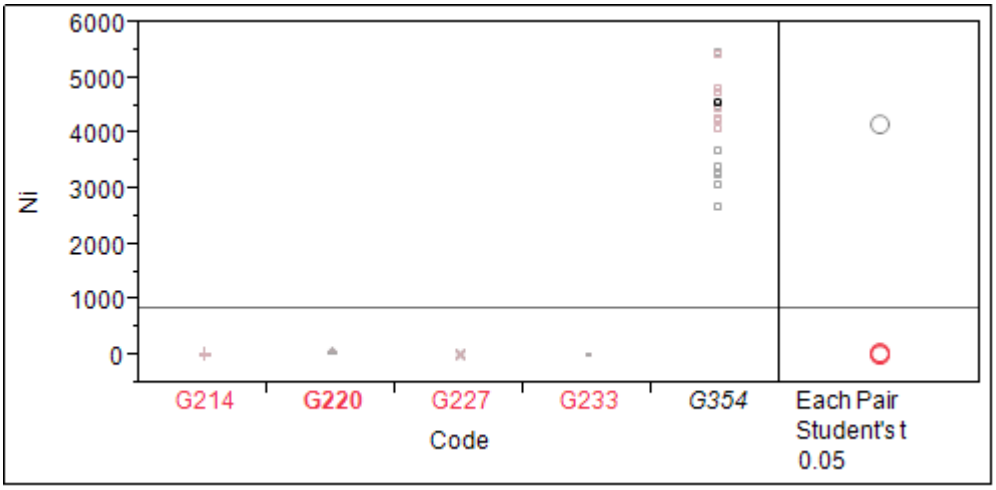

Figure 4.5: One way analysis of Ni content

Figure 4.6 shows the distribution pattern of Fe in various solder alloys, where the concentration of Fe is found in ppm level. It is believed that this impurity was not originate from raw material but was priminarily leached from melting pot into the molten solder during the melting process. In fact, the G345 samples are associated with the highest Fe contamination, $(0.07 \pm 0.03) \times 10^3$ ppm. This could be plausibly explained by the production of solder G345 (which consists of significant amount of Ni as shown earlier) generally requires a higher temperature than others and thus higher Fe was introduced.

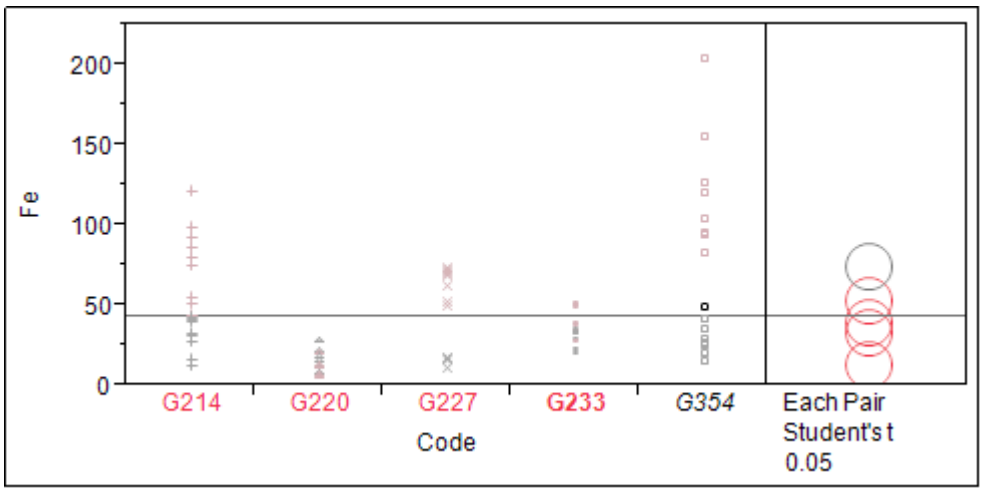

Figure 4.6: One way analysis of Fe content

Based on Figure 4.7, the Cu contents in the solder alloys can be categorized into 3 concentrations range (<500 ppm, 4000-6000 ppm, and 6000-7500 ppm) Cu was found as impurities in G214, G233 and G354 with concentartion less than 500 ppm. On the other hand, G220 and G227 found to be composed of (0.52 ± 0.02) % and (0.69 ± 0.02) % of Cu respectively. This mesurements will agree with the commersial solder alloys' specification if only G220 and G227 are donates to Sn96.5Ag3.0Cu0.5 and Sn99.3Cu0.7 respectvely.

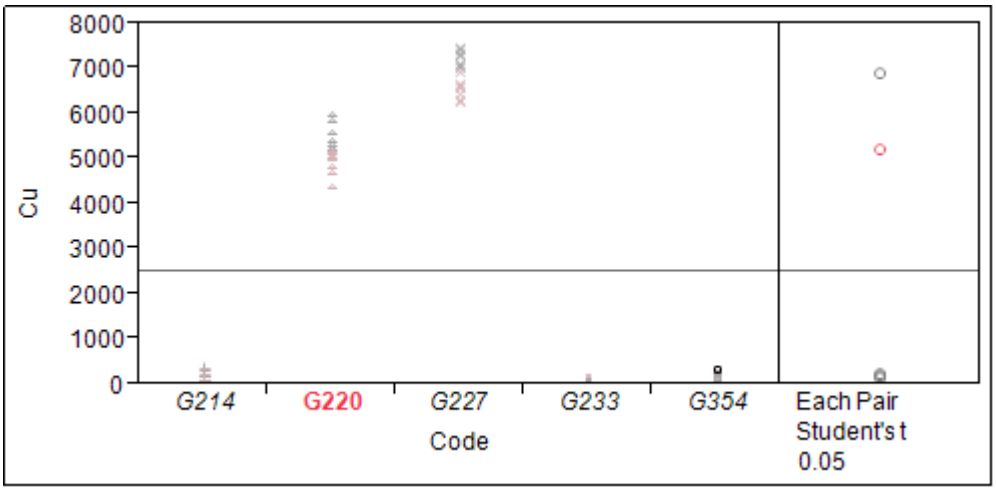

Figure 4.7: One way analysis of Cu content

Based on the results obtained by ICP-OES and spark emission spectroscopy, the concentration of Ag in solder samples are plotted in Figure 4.7. Higher Ag contents are found in G214, G220 and G354 compared to G227 and G233. In a glance, the Ag content there seems to be no considerable difference in G214, G220 and G354 as a result of high variation in the measurements contributed by various factor as mentioned before.

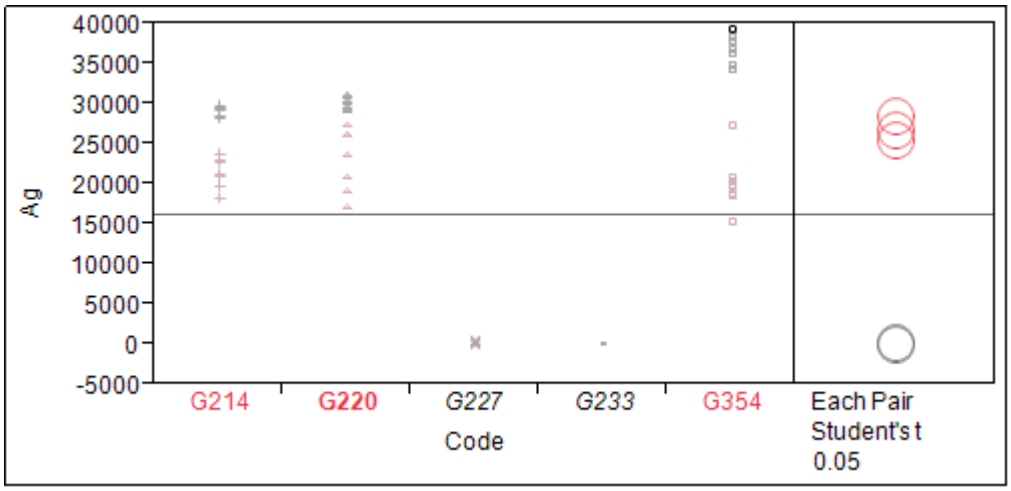

Figure 4.8: One way analysis of Ag content

Table 4.3 sum-ups the elemental compositions of the lead-free tin-based solder samples. In general, these solder alloys can be chemically characterized by the content of Ag, Cu and Ni which donates five different types of solder alloys as indicated by their code numbers. This finding is consistent with the results by HCA and PCA. Based these evidences, it can be deduced that the elemental compositions in the studied samples seem like in good agreement with the specifications of commercially available lead-free tin-based solder bar and/or solder wire as shown in Table 4.4.

However, Table 4.3 shows the Ag content of high silver content solder alloys as composition such as G220, G214, and G354 ((26.6 $\pm$ 2.1) X 10^3 ppm, (25.5 $\pm$ 2.0) X 10^3 ppm, (28.4 $\pm$ 4.4) X 10^3 ppm) is lower than expected which stated in Table 4.2 where G220

and G214 solder code should have 30 X 10^3 ppm of Ag; while 35 X 10^3 ppm for G354 solder code. Since Table 4.3 result is the sum up of Spark Emission and ICP-OES result, and ICP-OES contributing low Ag result due to the precipitation of AgCl from the reaction of Ag^+ and Cl^- from HCl.

On the other hand, from Table 4.3 which is the sum up elemental analysis results from spark emission and ICP-OES on Cu element for G220 and G227 are (5.2 ± 0.2) X 10^3 ppm and (6.9 ± 0.2) X 10^3 ppm. This is matching with the specification of the solder code G220 and G227 where their Cu concentration are 5.0 X 10^3 ppm and 7.0 X 10^3 ppm. This can be further conclude that there is no deviations on Cu elemental analysis between Spark Emission and ICP-OES.

Lastly, the sum up Ni analysis result from Spark Emission and ICP-OES for G354 solder alloy is (4.2 ± 0.4) X 10^3 ppm. This sum up result is matching with the specification of G354 solder alloy. However, it is slightly lower than expected. This is due to the low Ni being detected by Spark Emission due to the instrument is tuned lowly by using the only CRM which consist low Ni concentration that available.

Table 4.3: Elemental composition of solder alloy samples

Code	Concentration / × 10^3 ppm				
	Pb	**Ni**	**Fe**	**Cu**	**Ag**
G220	0.29 ± 0.03	0.042 ± 0.008	0.014 ±0.004	5.2 ± 0.2	26.6 ± 2.1
G214	0.18 ± 0.04	0.018 ± 0.009	0.054 ± 0.01	0.19 ±0.05	25.5 ± 2.0
G227	0.21 ± 0.04	0.032 ± 0.006	0.04 ± 0.01	6.9 ± 0.2	0.29 ± 0.07
G233	0.08 ± 0.03	0.015 ± 0.002	0.034 ± 0.004	0.13 ± 0.02	0.0025 ± 0.0009
G354	0.21 ±0.03	4.2 ± 0.4	0.07 ± 0.03	0.22 ± 0.02	28.4 ± 4.4

Table 4.4: The solder alloys' specification

Solder Code	Commercial Specification
G220	Sn96.5Ag3.0Cu0.5
G214	Sn97.0Ag3.0
G227	Sn 99.3Cu0.7
G233	Sn99.9
G354	Sn96.0Ag3.5Ni0.475

4.4 ICP-OES vs. Spark Emission Spectrometer

In general, Spark Emission Spectrometer that used (SpectroMaXx) is calibrated by tuning principle by using solid certified reference material (CRM) that manufactured by MBH analytical limited This tuning method is done by multiple-points sparking on the CRM where the corresponding intensities of targeted elemental wavelengths were adjusted so as to match the certified concentrations. In this context, the homogeneity of the CRM is definite a key factor that determines the tuning quality. In addition, the elemental concentration level available in the CRM is another concern. If the measured concentration much deviates from the tuning concentration, it leads to measurement bias. On the other hand, external calibration method is applied in ICP-OES analysis.

Although both of ICP-OES and Spark Emission are Optical Emission Spectrometry technique, but there are some agreement and deviation between ICP-OES analysis result and Spark Emission Spectrometer result. This is due to the sample being analyzed by these two techniques are in different form where sample preparation play a key role. Sample must be in solid form in order to be analyzed by Spark Emission Spectrometer; while the solid sample of solder need to be treated, digested and transform into solution form in order to introduced to sample introduction system of ICP-OES. There are many factors that may introduced during sample treatment which might affect the accuracy and precision of the result such as contamination, impurities of water, volatilization of analyte and etc.

4.4.1 Analysis of Ag in G220, G214 and G354

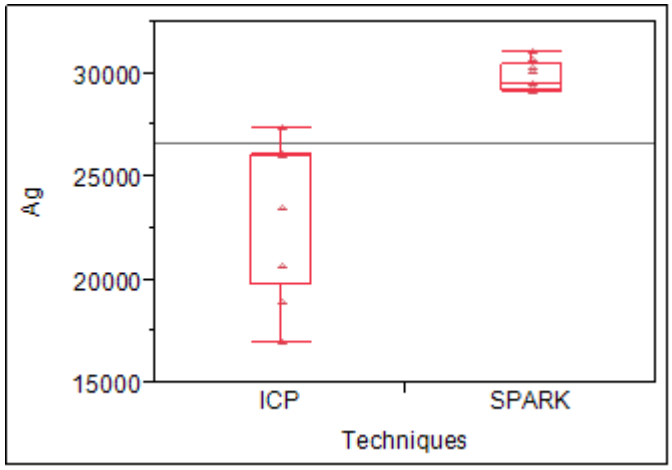

Figure 4.9: Ag Concentration in G220 solder alloy by Spark Emission and ICP-OES

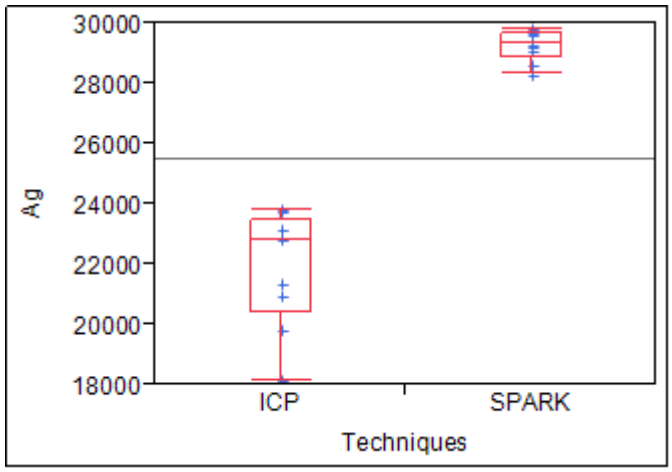

Figure 4.10: Ag Concentration in G214 solder alloy by Spark Emission and ICP-OES

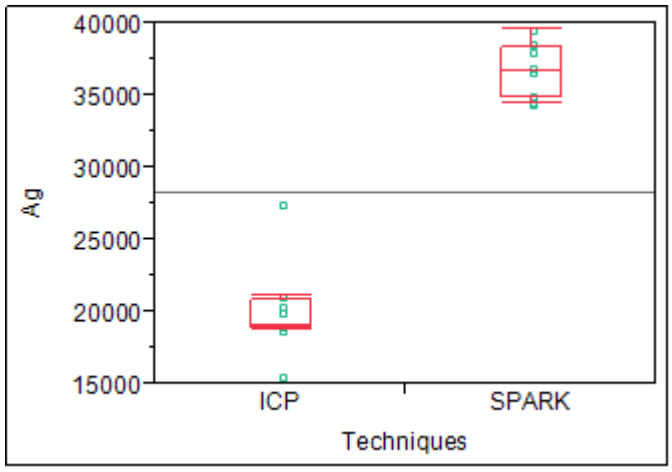

Figure 4.11: Ag Concentration in G354 solder alloy by Spark Emission and ICP-OES

Table 4.5: Ag detection in G220, G214, G354 solder alloy by Spark Emission and ICP-OES

Alloy code	Ag Concentration / X 10^3 ppm	
	Spark Emission	ICP-OES
G220	29.8 ±0.7	23 ±4
G214	29.2 ± 0.4	22 ±2
G354	37 ±2	20 ±3

Figure 4.9, Figure 4.10 and Figure 4.11 and Table 4.5 show Ag concentration detection by Spark Emission, and ICP-OES in G220, G214, G354 solder alloy respectively. These three figures and the table clearly show that the Ag being detected by ICP-OES technique is always lower than those detected by Spark Emission and lower than the average of sum up of Ag detection by both techniques. Besides that, Ag detection by ICP-OES is not precise as the results obtained are quite variable. This is because, in high Ag content solder alloy, silver element is forming silver chloride (AgCl) by reaction between Ag^+ from solder alloy with the Cl^- ion of Ar grade 37% HCl that used in the digestion

process. The rate and the amount formation of AgCl are very dependent on the volume of Ar grade 37%HCl that used. The higher the volume of HCl, the higher the amount AgCl formed, therefore the lower Ag concentration was determined by ICP-OES. The precipitation is not observed during the digestion process or even completion of digestion, it is only observed when the watch glass is rinsed with water and the solution is poured and filtered by filter paper. This is one of the reasons why we dint use ICP-OES technique to check and monitor the Ag concentration in solder alloy which can be easily determined by Spark Emission Spectrometer accurately and precisely. The only way to solve this problem is replace HCl by other reducing agent or using stroger acid such as HF.

4.4.2 Analysis of Cu in G220 and G227

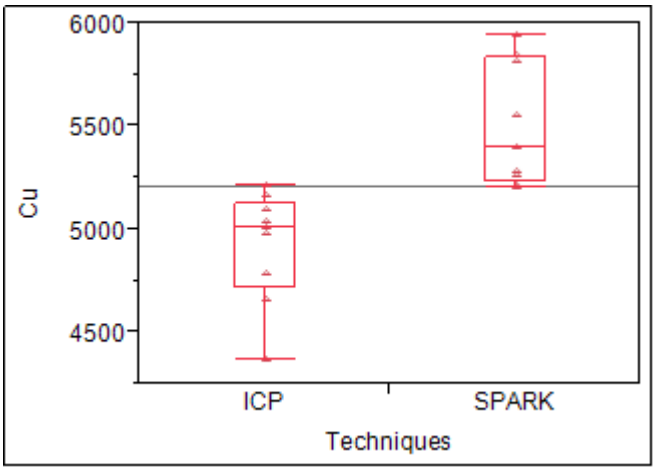

Figure 4.12: Cu Concentration in G220 solder alloy by Spark Emission and ICP-OES

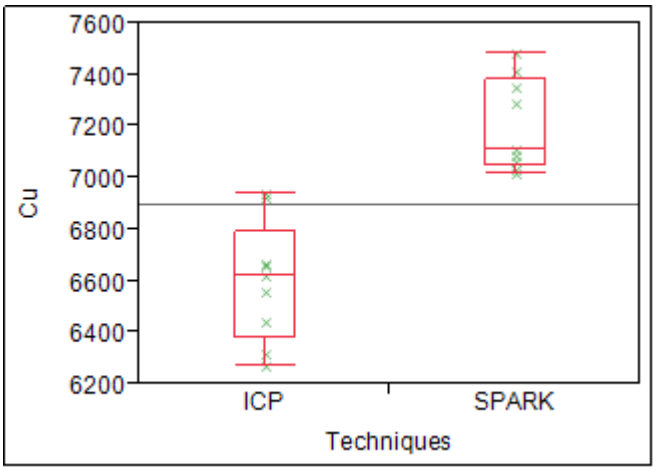

Figure 4.13: Cu Concentration in G227 solder alloy by Spark Emission and ICP-OES

Table 4.6: Cu detection in G220 and G227 solder alloy by Spark Emission and ICP-OES

Alloy code	Cu Concentration / X 10^3 ppm	
	Spark Emission	ICP-OES
G220	5.5 ±0.3	4.9 ±0.3
G227	7.2 ± 0.2	6.6 ±0.2

The graphs of Cu detection in G220 and G227 solder by Spark Emission and ICP-OES are shown in Figure 4.12 and Figure 4.13 respectively and their result's mean are summarized in Table 4.6. Form the figures, precision and the deviation of ICP-OES and Spark Emission are similar, however, ICP-OES result is slightly . This is due to the acid digestion process applied in ICP-OES technique where the Cu is evaporated during acid digestion and this evaporation is vary among the samples which depends on the size of the watch glass used in the digestion process. This evaporation of Cu also causes the result mean of Cu in both G220 and G227 solder alloy which detected by ICP-OES are always 0.6 X 10^3 ppm lower than Spark Emission technique

4.4.3 The Ni in G354

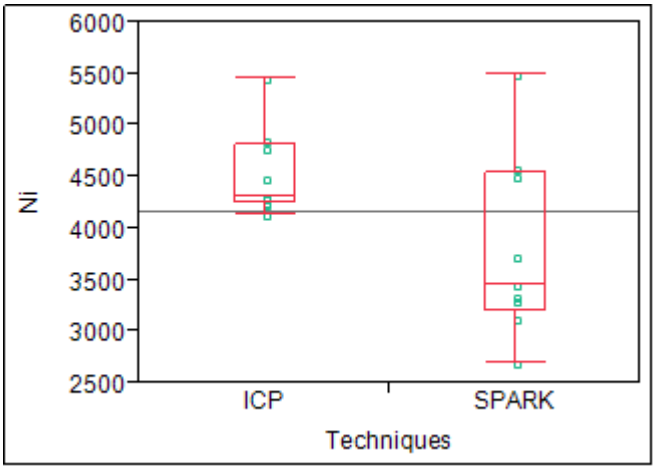

Figure 4.14: Ni Concentration in G354 solder alloy by Spark Emission and ICP-OES

Table 4.7: Ni detection in G354 solder alloy by Spark Emission and ICP-OES

Alloy code	Cu Concentration / X 10^3 ppm	
	Spark Emission	ICP-OES
G354	3.8 ±0.9	4.5 ±0.4

ICP-OES and Spark Emission result on Ni in G354 solder alloy are shown in Figure 4.14 and Table 4.7. Figure 4.13 shows that Spark Emission result on Ni in G354 solder alloy which contained high Ni is lower and more deviate if compared with ICP-OES result, where the standard deviation for This is because the Spark Emission Spectrometer CRM is containing low nickel concentration which is only 69ppm, therefore, it causes low nickel concentration is tuned to the particular wavelength, thus inaccurate result is given by extrapolating the calibration curve. Due to this reason, QC team used Spark Emission Spectrometer for screening and confirmed by ICP-OES since ICP-OES which based on external calibration principle could give more accurate and more precise result than Spark

Emission Spectrometer by preparing a series of external calibration standard and ensure the interest concentration is fall within the calibration curve.ICP-OES is 0.4 X 10^3 ppm; while Spark Emission has the deviation of 0.9 X 10^3 ppm.

4.4.4 Analysis of Fe in solder alloy

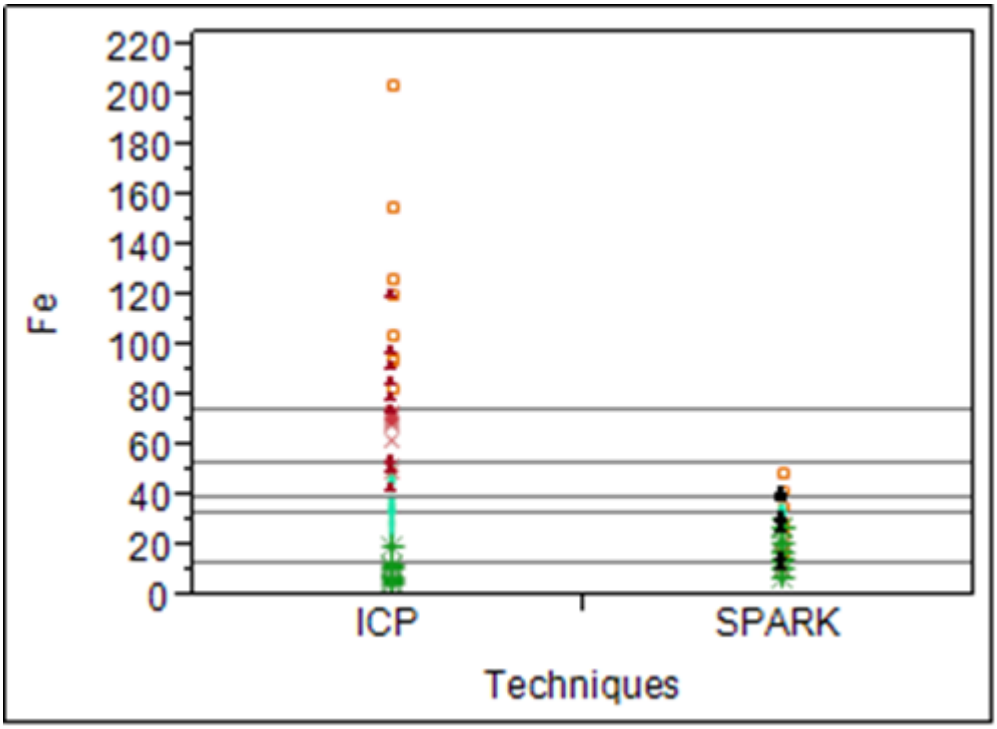

Figure 4.15: Distribution of Fe concentration in all type of solder alloys by Spark Emission Spectrometer and ICP-OES (G214: ▲; G354: □; G233: ▌; G227: x; G220: *)

From data obtained from Figure 4.15, generally, ICP-OES analysis has higher Iron (Fe) concentration than Spark Emission Spectrometer. This is due to the De-ionised water that used in the sample solution preparation of ICP-OES analysis is not pure enough which caused by the current resistivity is not high enough. The De-ionised water that generated by

the De-ionised water system that implemented in the laboratory is only could reach 4MΩ. This is far lower than the standard De-ionised water current resistivity which has the current resistivity of 18MΩ that should be used in ICP-OES analysis. Furthermore, Iron is present as impurities in the solder samples which exist in low concentration, this causes the contamination of iron from water influence the analysis result significantly. Besides, no frequent changing of filter cartridge worsens the contamination of Iron and affects the ICP-OES analysis result more significantly. However, analysis result shows that ICP-OES analysis of G220 solder alloy has lower Fe contents than those showed by Spark Emission Spectrometer. This may due to the filter cartridge was just changed right before the analysis of G220, therefore the resistivity resistant is higher and thus lower Fe contamination into the sample solution of G220 solder alloy Contamination is not from the both AR grade 37% HCl and AR grade 65% HNO_3 as water blank itself has high intensity of Iron peak. Figure 4.15 shows the distribution of Fe concentration in all type of solder alloys by Spark Emission Spectrometer and ICP-OES. This deviation can be corrected by comparison of CRM result of Spark Emission Spectrometer and ICP-OES technique and consider the difference between these two techniques so that we could know how much of Fe being contaminated from De-ionised water.

4.5 Wetting Balance Test

In wetting balance test, G354 has the longest wetting time for IC component at $250^{O}C$ among 5 solder alloys types due to less fluidity of the molten solder which caused by Ni although Ag in G354 helps in wettability. However, when the temperature is increased to $350^{O}C$, the fluidity of molten solder is thereby increase, hence, the wettability better than wettability at $250^{O}C$ as the wetting time is shortens from 0.65 second to 0.15second. On the other hand, there is no significant btw G220 and G214 on wetting time

for IC component at 250^{O}C due to the IC is not coated by Cu and appearance of Cu in G220 would not help in wettability. Next, the wettability of G227 and G233 is worse than G220 and G214 for IC component and it is the worst for copper coupon. However, among G233 and G227, there is no significant difference on wetting time of IC component. This is because IC component is not coated by Cu layer and Cu contents in the G227 will not help in wettability due to "Like dissolve Like" principle. On the other hand, G233 solder alloy has longer wetting time than G227 on half width copper coupon. This means that, G233 has worse wettability on half width copper coupon if compared with G227 solder alloy. However, it is no significant difference between them on full width copper coupon . This is due to insignificant effect of helpfulness of copper element from molten solder in "Like dissolve Like" principle. Due to this, G220 solder alloy which has 5000 ppm of copper always has better wettability on copper coupon than G214, regardless of full width or half width of copper coupon.

CHAPTER 5

CONCLUSION

Both ICP-OES and Spark Emission Spectrometer are not ideal techniques elemental analysis for all elements. ICP-OES is a better technique for analysis Ni at high concentration and Pb up to 500ppm. Meanwhile, Spark Emission Spectrometer is a better choice for analysis of Ag in high silver solder alloy, due to the contamination of Fe from water in sample preparation of ICP-OES analysis and precipitation of AgCl which formed by reaction between Ag^+ and Cl^- of HCl.

Although, ICP-OES is better choice in some circumstances, but, Spark Emission Spectrometer is first choice because of short analysis time is needed to monitor the composition and impurities of solder sample which taken from fast production process flow. This is important as production process pending for couple of hours just to obtain analysis result in order to proceed to next stage. However, ICP-OES is used to confirm nickel concentration for G354 solder alloy, and confliction of Pb contents between our result and customers' result.

New water system is necessary for ICP-OES as existing water system only able to generate 4MΩ current resistivity which is no good enough for ICP-OES analysis. This contributes Fe contamination into the analysis process and makes the analysis result inaccurate.

Development of new method is needed for ICP-OES Ag elemental analysis as AgCl is formed from the reaction between Ag^+ from analyte and Cl^- from HCl. Chemist need to get new acid which do not form precipitate with Ag and other analytes to digest the solder sample to improve ICP-OES analysis.

Wetting balance test shows that elemental composition such as Ag, Cu and Ni in solder alloy is affecting the wettability of molten solder, either shorten the wetting time or has longer wetting time. These results proves the literature review studies that used in this experiment.

References

A. D. Romig, Jr., Y. A. Chang, J. J. Stephens, D. R. Frear. V. Marcotte and C. Lea. (1991). CHAPTER 2 PHYSICAL METALLURGY OF SOLDER-SUBSTRATE REACTIONS. Solder Mechanics - A State of the Art Assessment. The Minerals, Metals & Materials Society. Pg 29-104.

AI-PING XIAN and GUO-LIANG GONG. (2007). Oxidation Behavior of Molten Tin Doped with Phosphorus. Journal of Electronic Materials, Vol. 36, No. 12. Pg1669-1678.

C. S. Chew, A. S. M. A. Haseeb, M. R. Johan. (2009). Wetting Behaviour of Lead Free Solder on Electroplated Ni and Ni-W Alloy Barrier Film. *International Conference on Electronic Packaging Technology & High Density Packaging*. Pg 795-798.

Carol Handwerker, Ursula Kattner, Kil-Won Moon (2007) Chapter 2: Fundamental Properties of Pb-Free Solder Alloys. Pg 31-36.

Christopher M. Carabello (1998) LEAD-FREE SOLDER. RedRingSolder (M) Sdn. Bhd.

Deubzer, O., Nissen, N.F., Lang, K.-D. (2012). Overview of RoHS 2.0 and status of exemptions. *Electronics Goes Green 2012+ (EGG). V*ol.30, no.3, pp.1-6.

Drag soldering. (2013). Available: http://www.howardelectronics.com/jbc/dragsoldering.html Last accessed 07-10-2013.

Dunnivant and Ginsbach, 2009 Inductively Coupled Plasma—Atomic Emission Spectrometry Available: http://people.whitman.edu/~dunnivfm/FAASICPMS_Ebook/Downloads/. Last Accessed 22-03-2014.

Eric Bastow (2005). *Solder families and they work.* Available: http://www.ostec-materials.ru/upload/iblock/714/71418246221db5e84a71e8973b38f94e.pdf Last accessed 14-09-2013.

Gary Solomon. (2014). Process integration of electroplated solder bumps for WLP. Available: (http://electroiq.com/blog/2001/11/process-integration-of-electroplated-solder-bumps-for-wlp/ Last accessed 02-01-2014.

Gilleo Ken (2004). The First 7,000 Years of Soldering, *Part I Circuits Assembly October*, Pg 30-34.

Hard Soldering (07-09-2013) Available: http://chestofbooks.com/crafts/mechanics/How-To/Hard-Soldering.html#.UkEoTdKma-k Last accessed 24-09-2013.

Hisaaki Takao, Toshihiko Tsukada, Keiichi Yamada,Masahiko Yamashita, Hideo Hasegawa (2004) . Development of Wettability Evaluation Technique Applying Contact Angle Measurement during Soldering. *R&D Review of Toyota CRDL* Vol. 39 No. 2. Pg41-48.

How to Solder Glass Pendants (2013) Available: http://www.rings-things.com/blog/tag/soft-solder/#.Ui7If9Kma-k Last accessed 10-09-13.

Jeff D. Sigelko* K. N. Subramanian (2001). *Overview of lead-free solder*. Pg1-2.

Jerry C. Septon (1993*). ICP Backup Data Report for Soldering & Brazing Matrices (ARL 3560)*. Available: https://www.osha.gov/dts/sltc/methods/inorganic/id206arl3560icp/id206arl3560icp.html Last accessed 07-10-2013.

Joe Fjelstad. Brief history of solder in Electronic assembly. (2011) Available: http://www.pcb007.com/pages/zone.cgi?a=74537 Last accessed 14-09-2013.

Jung H. Kim, Jihye Lee, and Choong D. Yoo. (2005). Soldering Method Using Longitudinal Ultrasonic. *IEEE TRANSACTIONS ON COMPONENTS AND PACKAGING TECHNOLOGIES*, VOL. 28, NO. 3, SEPTEMBER 2005 pg 493-498.

Karl J. Puttlitz, Kathleen A. Stalter. (2004). Handbook of lead-free solder technology for microelectronic assemblies. *CRC Press*. p. 541.

M. Bent and G. Solomon. (2001). Using Wet Chemistry for Etching Under Bump Metal. *Solid State Technology*. pp. 89-92.

Mark J. Hoban and Barry M. Lunt (1997). *SOLDERING*. Available: http://technologyinterface.nmsu.edu/spring97/electronics/solder/solder.html Last accessed 14-09-2013.

Ngoc Binh Duong, Tadashi Ariga, Luay Bakir Hussain and Amad Badri Ismail. (2008). Wettability of Lead-Free Solders on Gold-Plated Copper Substrates. *Materials Transactions*. Vol. 49, No. 6, pp. 1462 to 1466.

Norhazlina Ismail & Jong Yoo. (2003). Determination of Lead (Pb) Concentration Level in Solder Finished Product Using Laser Induced Breakdown Spectroscopy (LIBS). Electronics Packaging Technology Conference European Comission, "Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment". Official Journal of the European Union, February, 2003. pg 456-461.

OPTICAL EMISSION SPECTROSCOPY. (1998). *Comalco Technical Report*. No. 5. Pg 3-10.

Qian Sun and G. Selvaduray. (2003). Understanding and Minimization of Tin Whiskers a review of the literature. *San Jose State University Seminar June 2013*.

Qinghua Zhao, Zhuo Chen, Anmin Hu, Ming Li. (2013). Formation of SnAg solder bump by multilayer electroplating. Microelectronic Engineering. Volume 106, pages 33-37.

QUANTITATIVE CHEMICAL ANALYSIS 2010. Handbook of analytical methods for materials. Materials Evaluation and Engineering, Inc. pg31-34. Available: http://mee-inc.com/hamm72d.pdf. Last accessed 23-03-2014.

Recommended Soldering Techniques (2013) AP02014 Rev. 02 Available: http://www.diodes.com/pdfs/Ap02014_R1_Soldering.pdf Last accessed 07-10-2013.

RoHS Regulation. (2011). Government Guidance Note. Available: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/31803/11-526-rohs-regulations-government-guidance-notes.pdf Last accessed 06-05-2014.

Silver Soldering (2013) Available: http://www.uvm.edu/safety/art/silver-soldering Last accessed 25-09-2013.

Soft Solder Information (2009). Available: http://metalli.com/index.php?option=com_virtuemart&page=shop.browse&category_id=66&Itemid=29&TreeId=25 Last accessed 08-09-2013.

Soft soldering (2011) Available: http://www.steves-workshop.co.uk/tips/softsoldering/solderingindex.htm Last accessed 08-09-2013.

Soft Soldering Handbook (5th Edition) (2001) Tin Technology Limited. Pg1-3

Solder (2013). Available: http://en.wikipedia.org/wiki/Solder Last accessed 06-09-13.

Solder (2013). Merriam-webster dictionary. Retrieved on 14-09-2013, from: http://www.merriam-webster.com/dictionary/solder.

Solder alloys (2009) Available: http://www.keytometals.com/page.aspx?ID=CheckArticle&site=ktn&NM=229 Last accessed 25-09-2013.

Solder Types (2013). Available: http://www.efunda.com/materials/solders/types.cfm Last accessed 06-09-13.

Solder Types and Uses The Categories and Correct Choice (2009). Available: http://www.ebay.com/gds/Solder-Types-and-Uses-The-Categories-and-Correct-Choice-/10000000009978441/g.html Last accessed 06-09-13.

Soldering 101 (2013). Available: http://www.rings-things.com/resources/solder.html#.Uix46sbik5M Last accessed 08-09-2013.

Soldering and Brazing (2008). Available: http://www.northsearegion.eu/files/repository/20130821115216_WP_2_Inventory_Technologies_VHS_Hamburg.pdf Last accessed 06-10-2013.

Soldering and Brazing (2013). Available: http://www.ignou.ac.in/upload/Unit-6.pdf Last accessed 07-10-2013.

Soldering history. (2013). Available: http://www.ersa.com/soldering-history-en.html. Last Accessed 14-09-2013.

Soldering methods and procedures for Vicor Power Modules (2013) Available: http://www.vicorpower.com/documents/application_notes/an_powermodulesoldering.pdf Last accessed 07-10-2013.

Yosuke MORISHIGE and Atsushi KIMURA. (2008). Ionization Interference in Inductively Coupled Plasma- Optical Emission Spectroscopy. SEI TECHNICAL REVIEW ·NUMBER 66. pg 106-111.

Yun Zhang. (2010). TIN AND TIN ALLOYS FOR LEAD-FREE SOLDER. Modern Electroplating. Fifth Edition. Pg 139-204.

Appendices

4.1 Spark Emission Spectrometer

Table 1: Elemental analysis result of G220

	Concentration (ppm)								
Elements	G220								
	1309654			1309657			1310732		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
Pb	260	264	225	340	339	335	372	367	349
Ni	60	61	59	25	27	25	39	38	38
Fe	27	28	27	11	11	7.3	15	18	21
Cu	5400	5550	5280	5260	5210	5200	5940	5820	5840
Ag	30700	31000	30300	29100	29300	29100	30100	29300	29500

Table 2: Elemental analysis result of G214

	Concentration (ppm)								
Elements	G214								
	1305285			1310701			1310729		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
Pb	149	149	144	154	156	156	315	305	305
Ni	10	10	10	23	23	23	27	28	28
Fe	16	16	13	42	27	41	31	40	32
Cu	78	83	81	166	158	169	292	273	289
Ag	29300	29400	29100	28600	29200	28300	29800	29700	29600

Table 3: Elemental analysis result of G227

	Concentration (ppm)								
Elements	G227								
	1306415			1306449			1308618		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
Pb	133	141	141	312	289	320	168	179	173
Ni	28	24	30	49	47	49	22	22	22
Fe	11	11	11	16	16	17	16	18	17
Cu	7060	7110	7090	7410	7020	7480	7030	7350	7290
Ag	25	24	27	223	206	230	367	399	382

Table 4: Elemental analysis result of G233

	Concentration (ppm)								
Elements	G233								
	1310755			1310760			1310768		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
Pb	163	163	168	22	21	21	42	41	38
Ni	17	16	16	9.8	8.8	9.4	11	11	9.4
Fe	22	29	20	35	33	32	34	29	33
Cu	106	99	101	87	79	83	100	101	84
Ag	6.0	6.2	6.0	0.5	0.5	0.5	1.7	1.3	1.3

Table 5: Elemental analysis result of G354

	Concentration (ppm)								
Elements	G354								
	1308587			1311793			1311818		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
Pb	286	283	275	248	266	267	250	264	269
Ni	3290	3450	3340	3730	3120	2700	5490	4510	7580
Fe	30	26	27	16	21	28	36	42	50
Cu	198	192	200	188	163	166	247	200	350
Ag	36900	36600	36600	34600	35000	34400	38600	38000	39600

4.2 ICP-OES

Table 6: Elemental analysis result of G220

	Concentration (ppm)											
Elements	G220											
	1309654				1309657				1310732			
	blank	S1	S2	S3	blank	S1	S2	S3	blank	S1	S2	S3
Pb	0.014	200.5	249.4	197.7	0.013	218.7	271.9	294.8	0.018	306.3	295.5	266.6
Ni	0.005	68.40	65.21	61.93	0.018	25.35	27.63	26.95	0.031	36.39	39.64	35.72
Fe	0.02	19.87	12.11	19.96	0.04	5.29	5.37	7.38	0.08	5.91	10.97	4.74
Cu	0.005	4976	4656	4781	0.004	4364	5006	5163	0.003	5211	5037	5091
Ag	0.052	26120	25950	20680	0.049	16940	27360	23420	0.046	25940	25940	18922

Table 7: Elemental analysis result of G214

	Concentration (ppm)											
Elements	G214											
	1305285				1310701				1310729			
	blank	S1	S2	S3	blank	S1	S2	S3	blank	S1	S2	S3
Pb	0.009	132.8	97.77	102.8	0.007	108.6	138.9	113.3	0.019	275.8	236.2	240.7
Ni	0.003	2.049	2.191	1.884	0.011	17.15	20.46	17.98	0.034	27.36	25.46	25.70
Fe	0.147	44.01	51.83	55.18	0.196	99.13	92.50	121.0	0.139	79.48	86.38	75.44
Cu	0.022	76.86	89.61	86.31	0.061	211.9	194.2	217.4	0.051	339.5	333.6	325.9
Ag	0.058	21320	23800	22810	0.084	18160	19790	23760	0.042	23080	23110	20960

Table 8: Elemental analysis result of G227

	Concentration (ppm)											
Elements	G227											
	1306415				1306449				1308618			
	blank	S1	S2	S3	blank	S1	S2	S3	blank	S1	S2	S3
Pb	0.005	140.3	142.5	140.6	0.004	273.9	305.6	302.0	0.005	181.0	181.1	180.6
Ni	0.002	23.96	33.62	27.94	0.008	46.15	45.02	45.11	0.013	18.50	20.59	19.35
Fe	0.143	52.55	62.38	50.60	0.158	72.87	73.40	72.29	0.166	68.70	69.86	71.21
Cu	0.008	6445	6268	6558	0.008	6656	6938	6922	0.009	6318	6621	6664
Ag	0.016	358.3	343.2	353.1	0.016	382.7	380.5	373.5	0.022	369.2	350.6	337.0

Table 9: Elemental analysis result of G233

	Concentration (ppm)											
Elements	G233											
	1310755				1310760				1310768			
	blank	S1	S2	S3	blank	S1	S2	S3	blank	S1	S2	S3
Pb	0.004	171.3	170.0	168.3	0.007	27.78	27.33	36.46	0.008	43.63	43.49	43.10
Ni	0.004	19.34	18.78	20.07	0.006	16.82	16.47	16.51	0.001	16.57	18.24	17.82
Fe	0.153	27.66	34.28	27.30	0.153	38.16	37.50	37.37	0.182	49.55	50.81	48.46
Cu	0.09	176.3	174.9	174.2	0.069	162.2	161.0	161.0	0.077	167.4	173.9	172.3
Ag	0.018	1.524	1.639	1.525	0.021	1.735	1.725	1.735	0.018	3.516	3.416	3.523

Table 10: Elemental analysis result of G354

	Concentration (ppm)											
Elements	G354											
	1308587				1311793				1311818			
	blank	S1	S2	S3	blank	S1	S2	S3	blank	S1	S2	S3
Pb	0.012	161	185.6	186.8	0.016	152.7	169.2	123.3	0.007	121.8	118.7	114.1
Ni	0.015	4249	4132	4487	0.016	4238	4782	4316	0.017	5453	4293	4846
Fe	0.206	156.3	205.1	104.9	0.290	121.1	127.0	95.73	0.250	94.93	83.60	83.27
Cu	0.053	229.3	228.7	226.5	0.058	229.8	221.7	223.5	0.049	272.2	217.8	242.6
Ag	0.024	18730	27520	19090	0.082	20040	21100	15540	0.021	19090	20480	18980

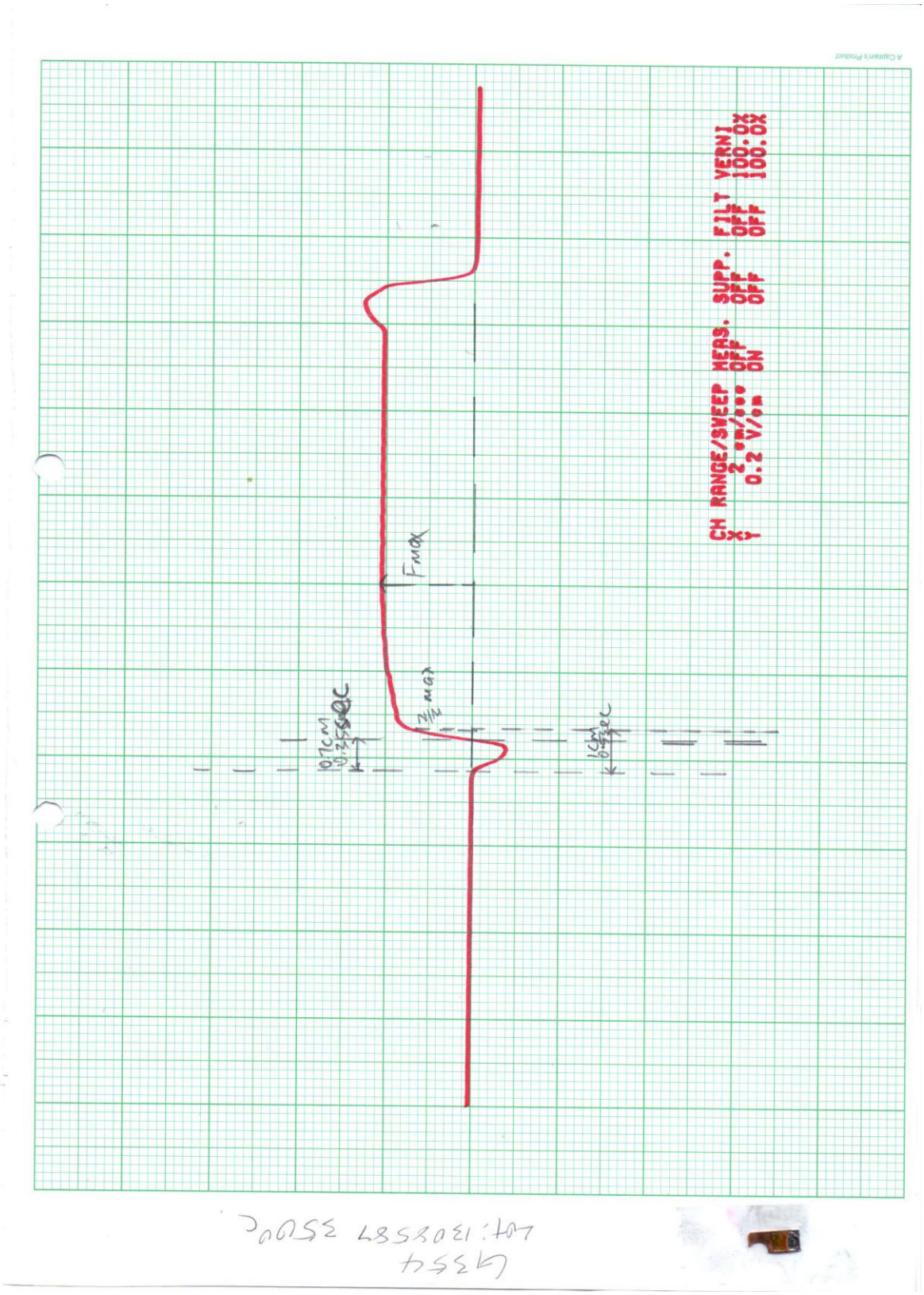

Figure 1: Wetting balance curve for half width copper specimen on G354 solder alloy at 350^{O}C

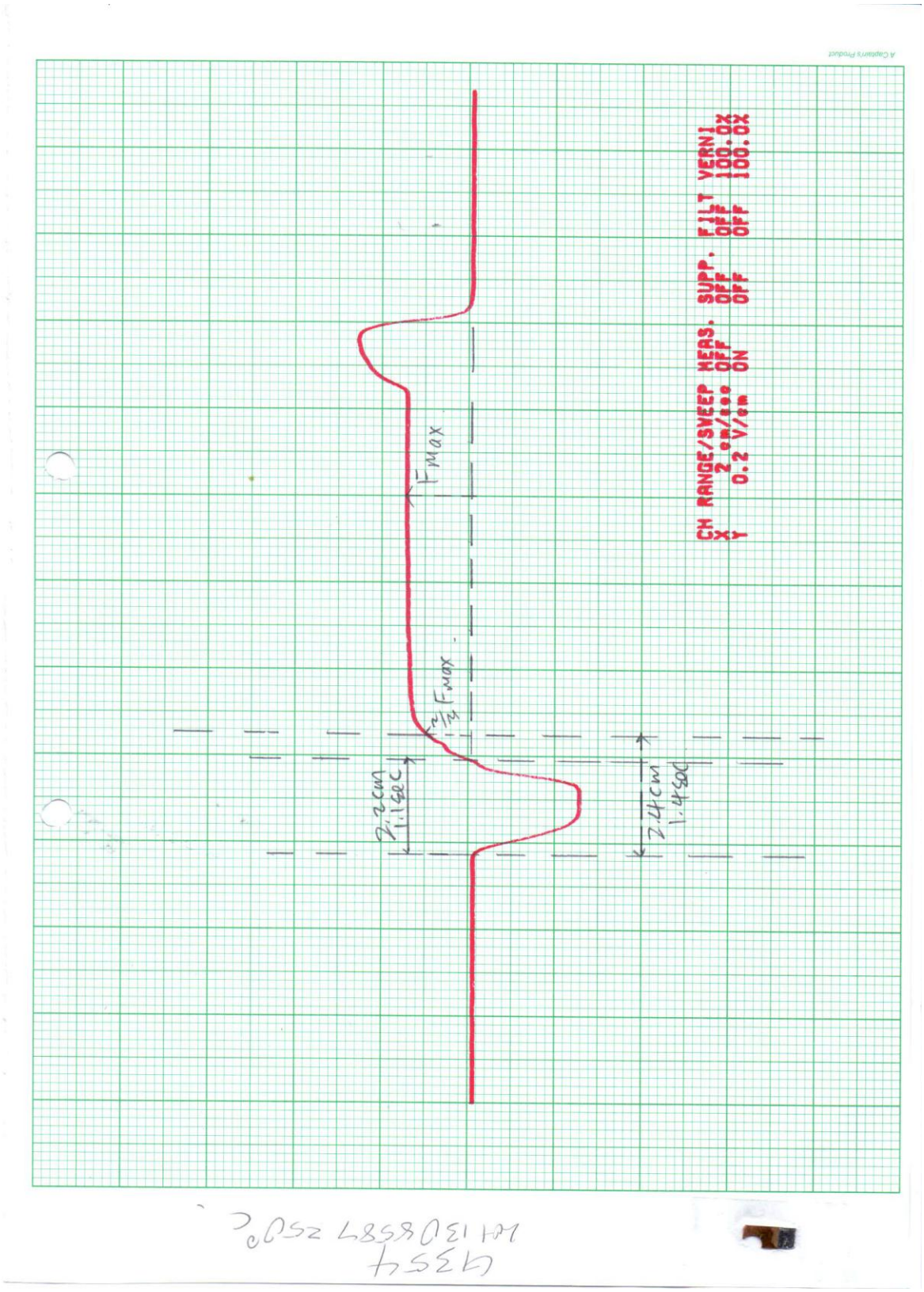

Figure 2: Wetting balance curve for half width copper specimen on G354 solder alloy at 250^{O}C

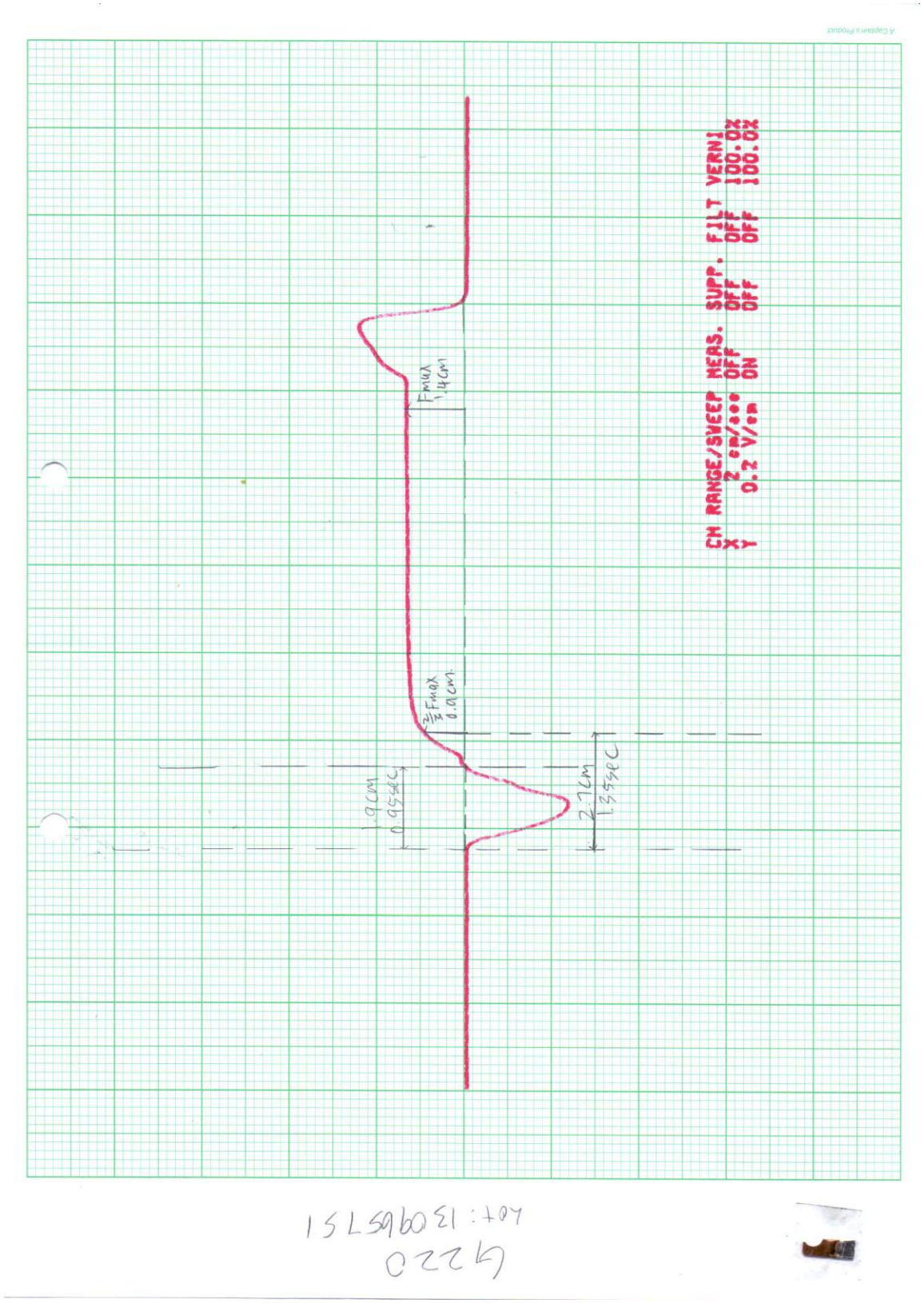

Figure 3: Wetting balance curve for half width copper specimen on G220 solder alloy at 250^{O}C

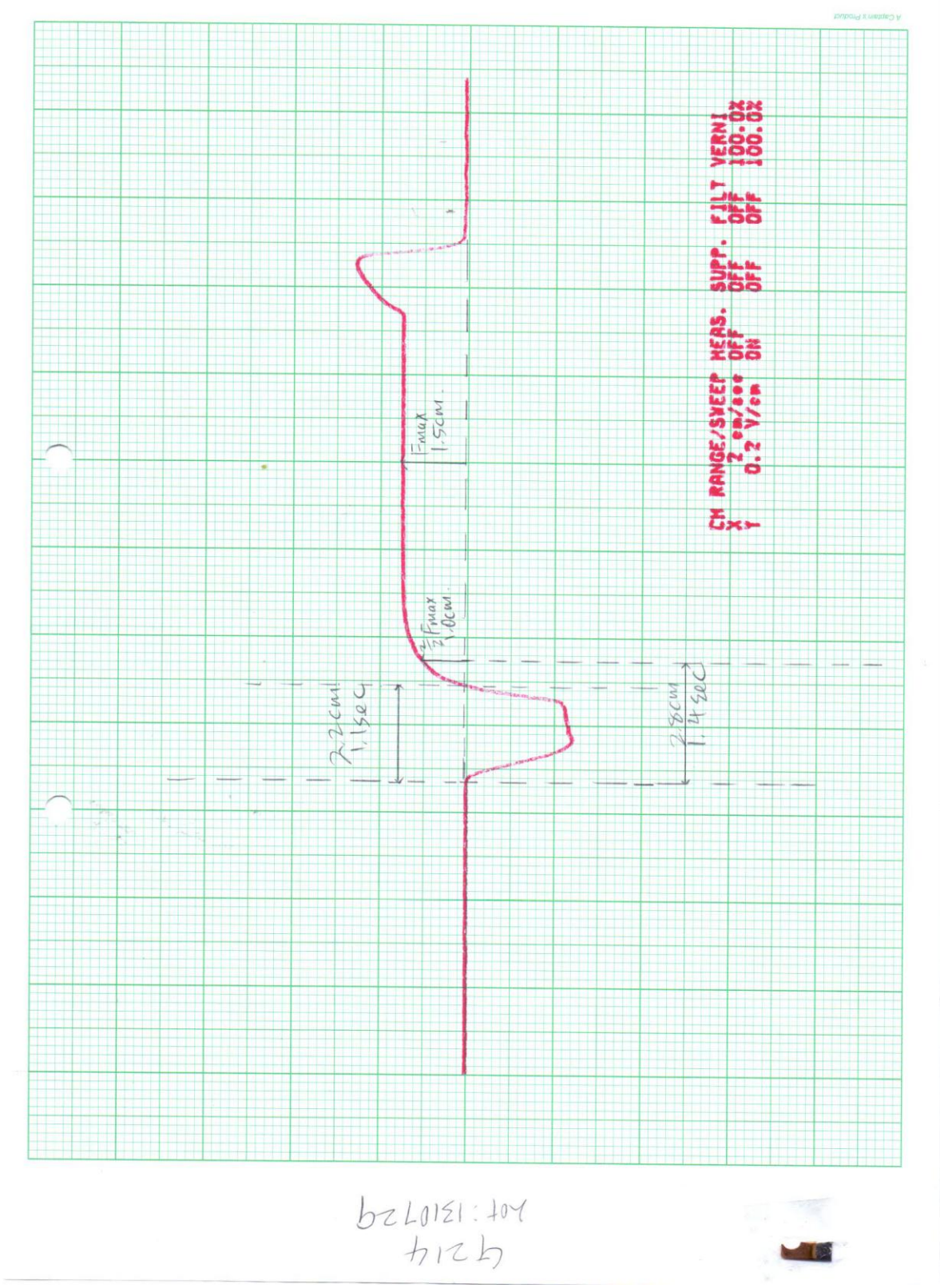

Figure 4: Wetting balance curve for half width copper specimen on G214 solder alloy at 250^{O}C

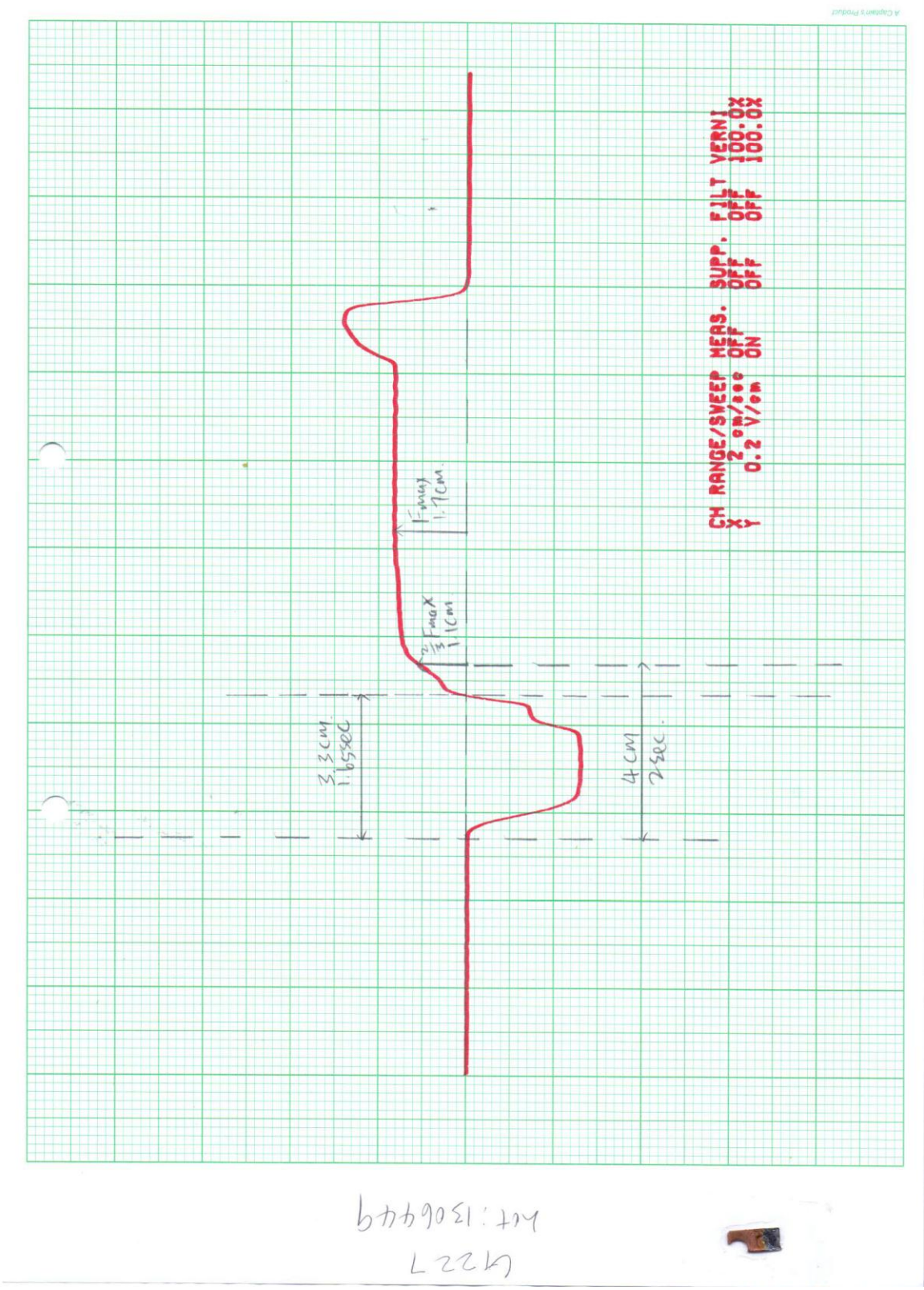

Figure 5: Wetting balance curve for half width copper specimen on G227 solder alloy at 250^{O}C

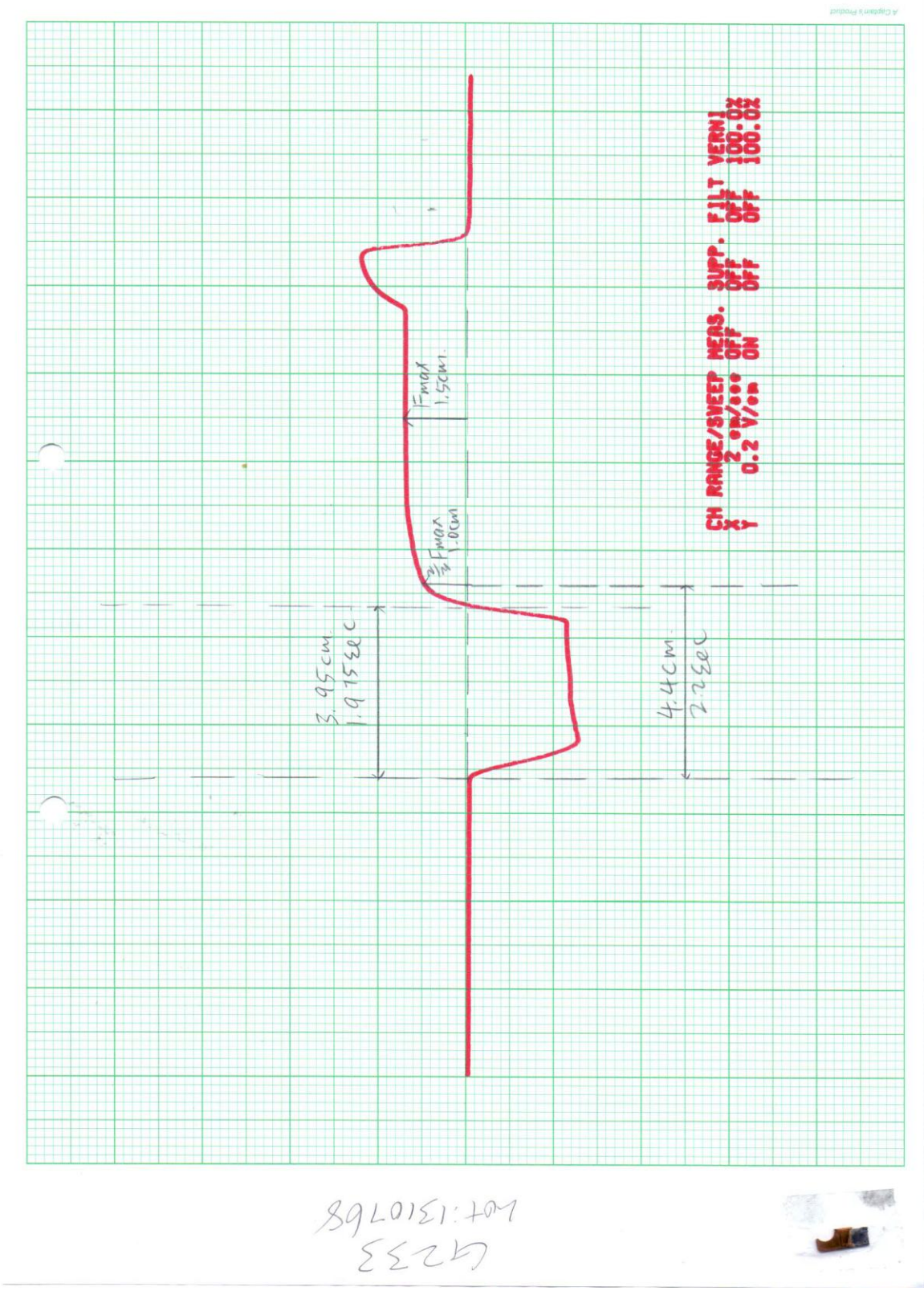

Figure 6: Wetting balance curve for half width copper specimen on G233 solder alloy at 250^{O}C

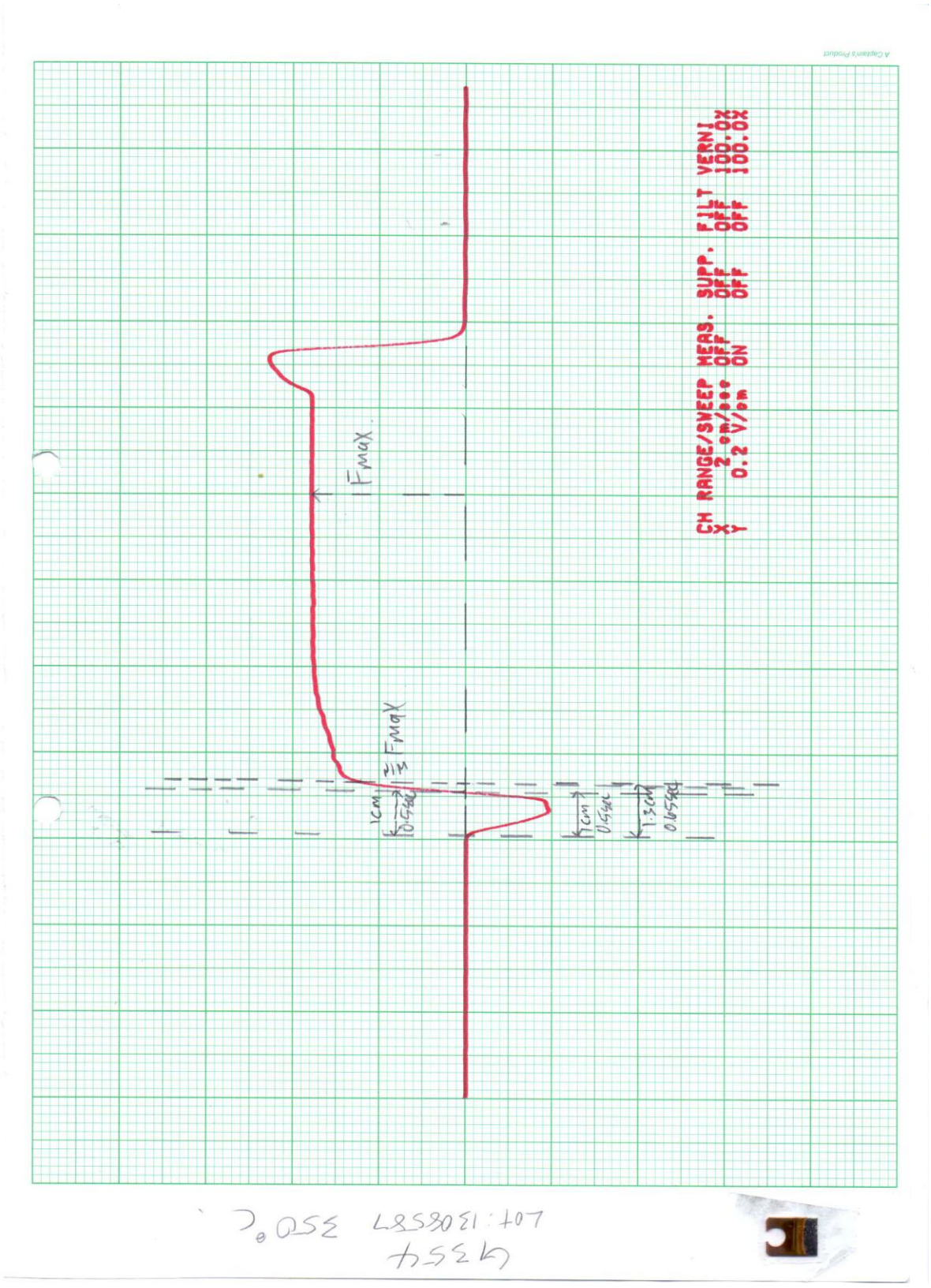

Figure 7: Wetting balance curve for full width copper specimen on G354 solder alloy at 350^{O}C

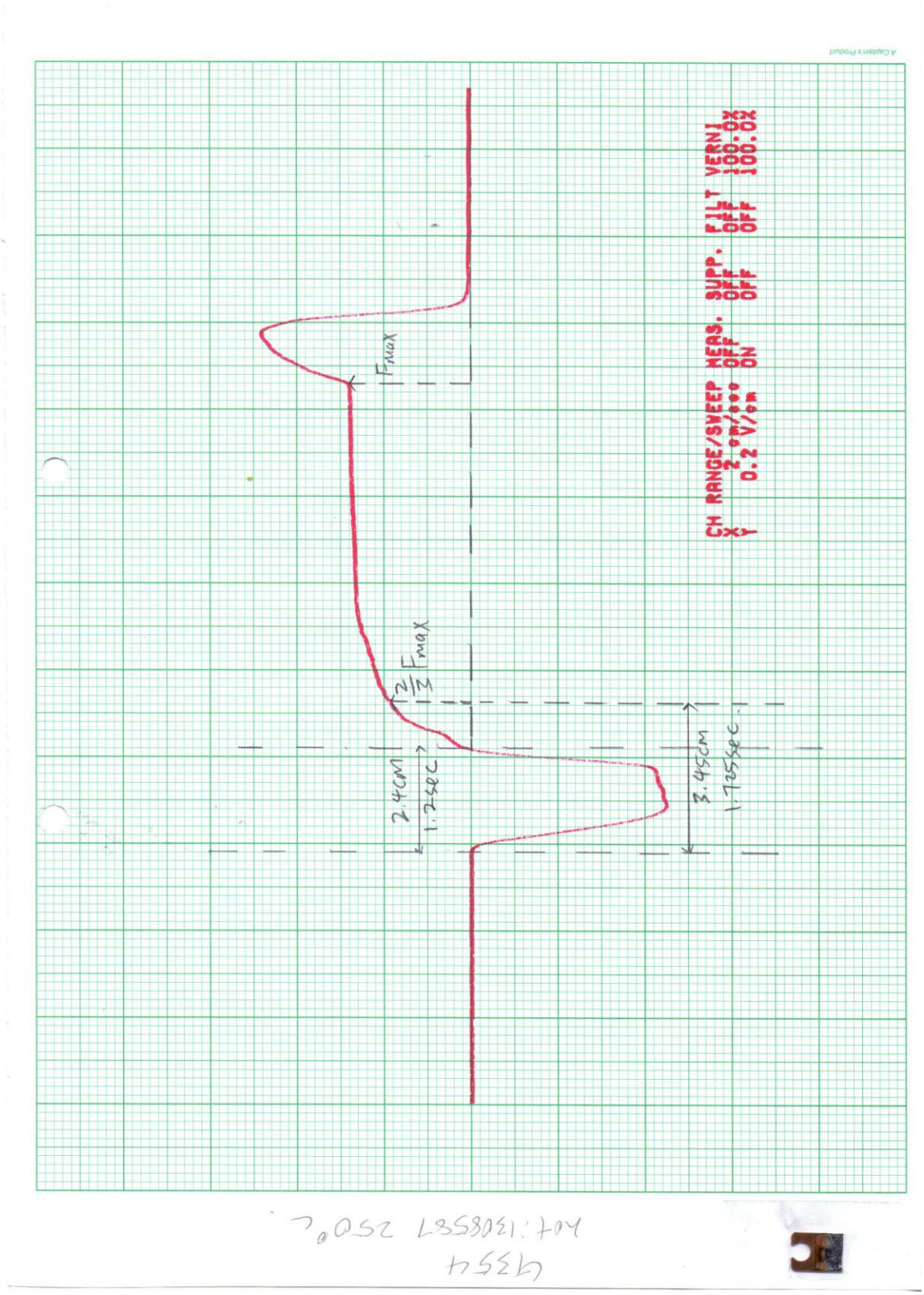

Figure 8: Wetting balance curve for full width copper specimen on G354 solder alloy at 250^{O}C

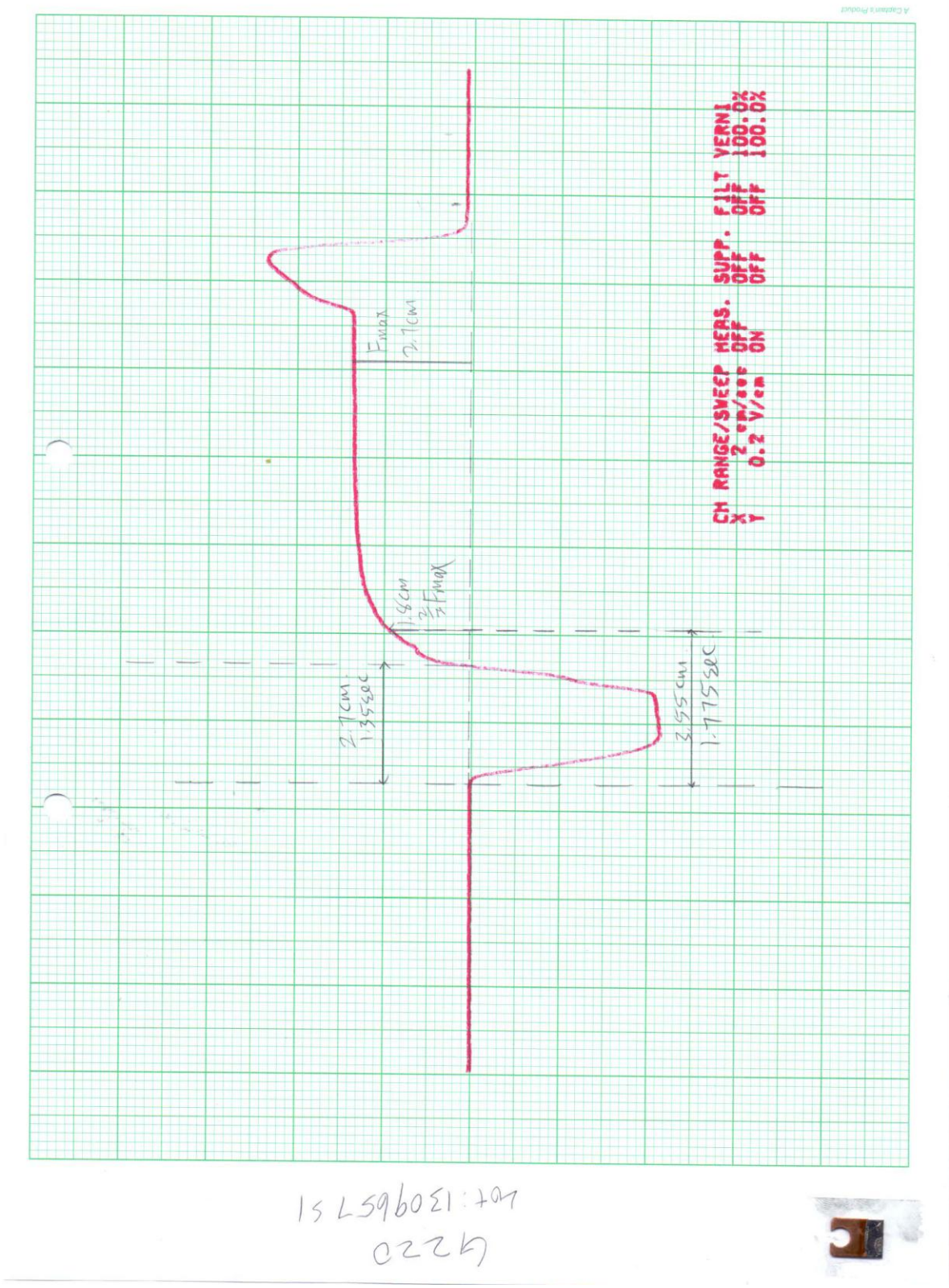

Figure 9: Wetting balance curve for full width copper specimen on G220 solder alloy at 250^{O}C

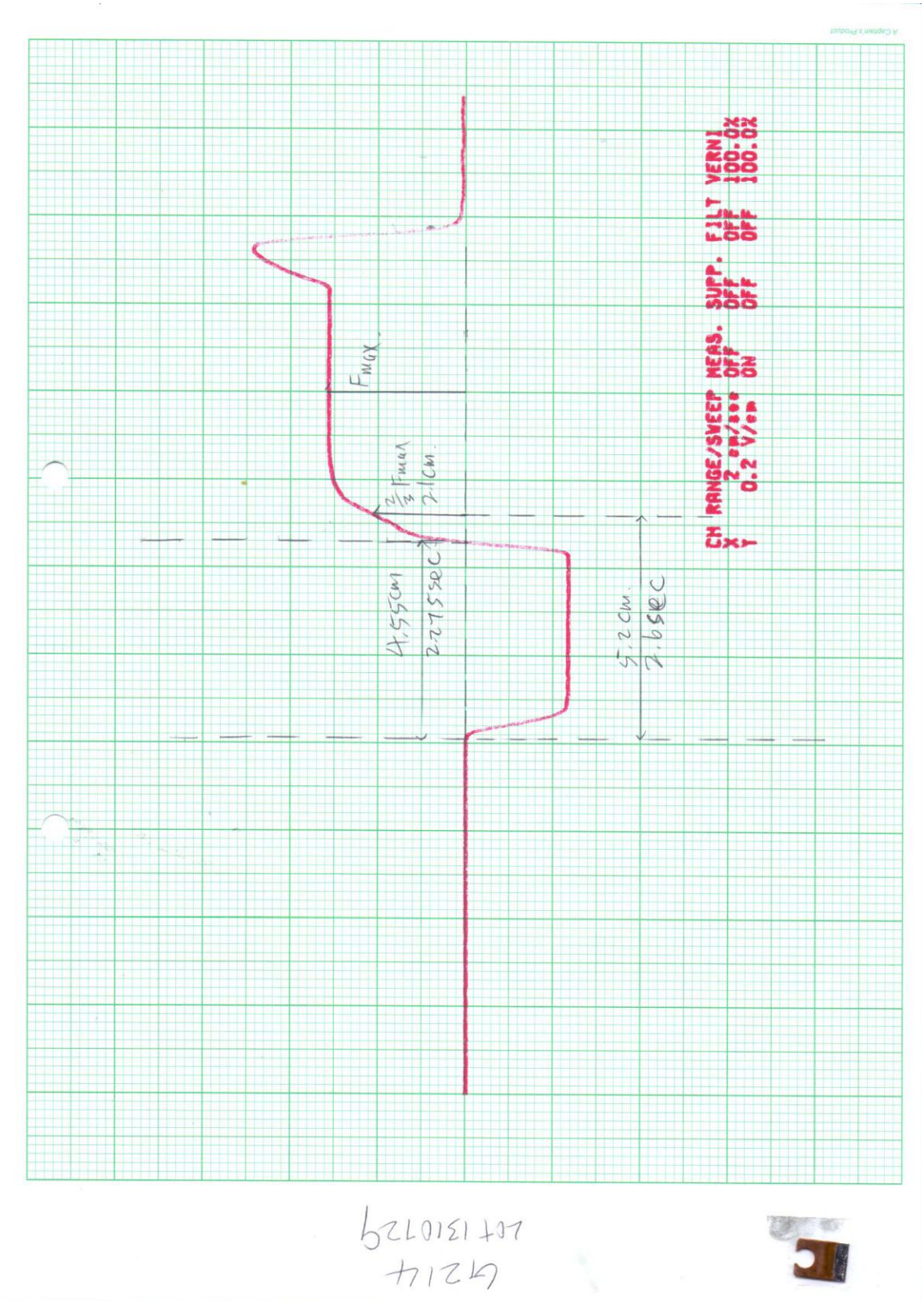

Figure 10: Wetting balance curve for full width copper specimen on G214 solder alloy at 250^{O}C

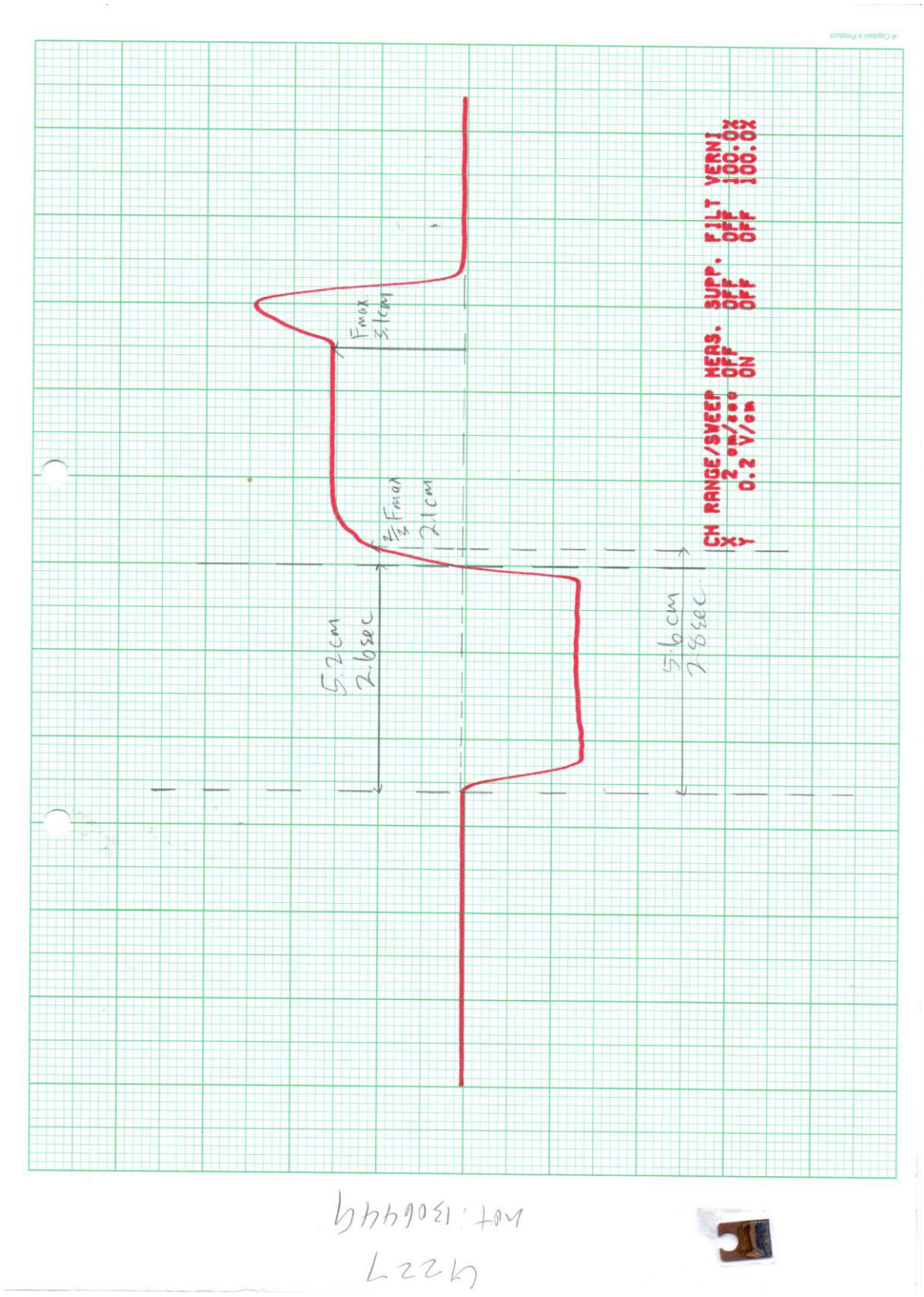

Figure 11: Wetting balance curve for full width copper specimen on G227 solder alloy at 250^{O}C

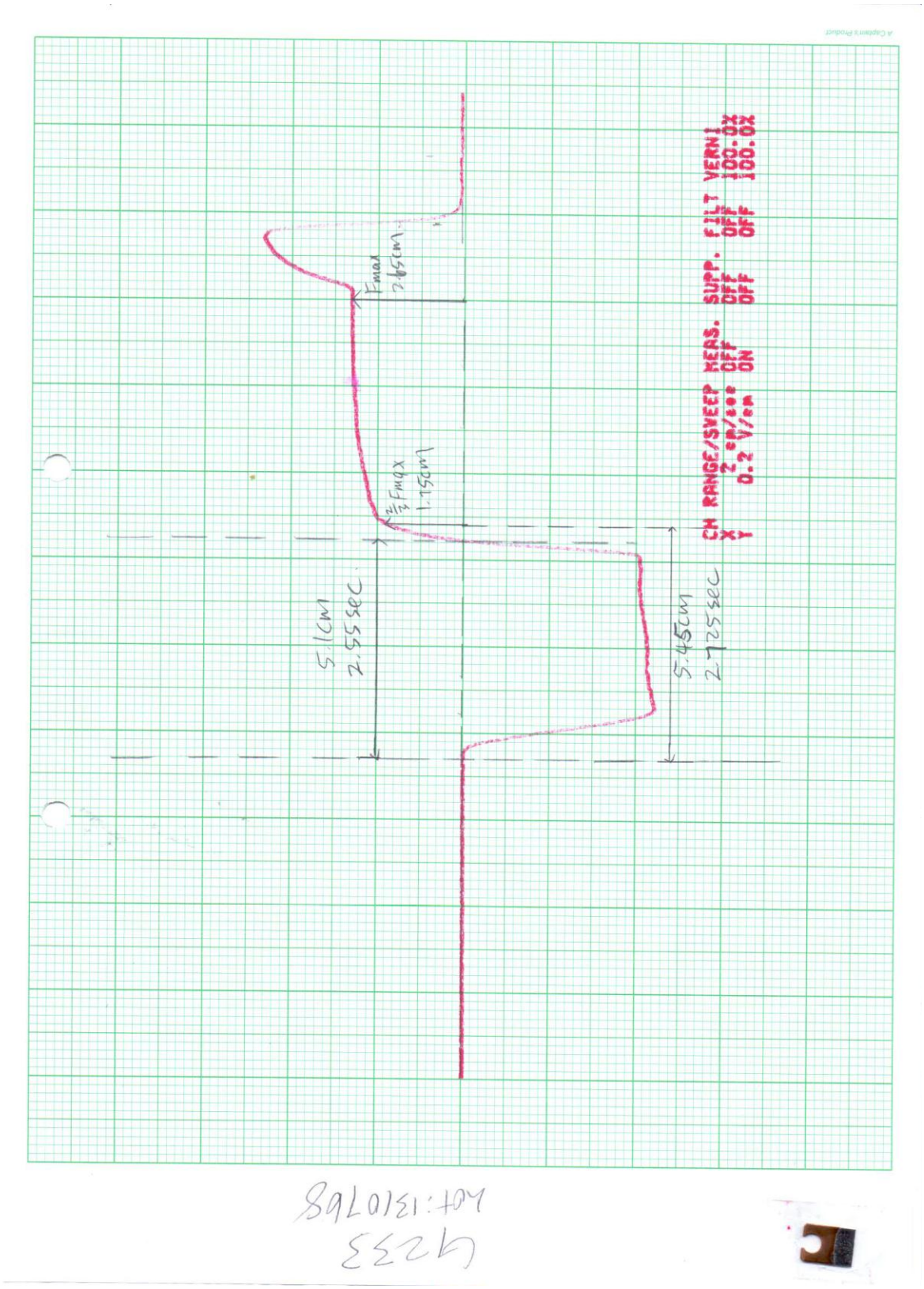

Figure 12: Wetting balance curve for full width copper specimen on G233 solder alloy at 250^{O}C

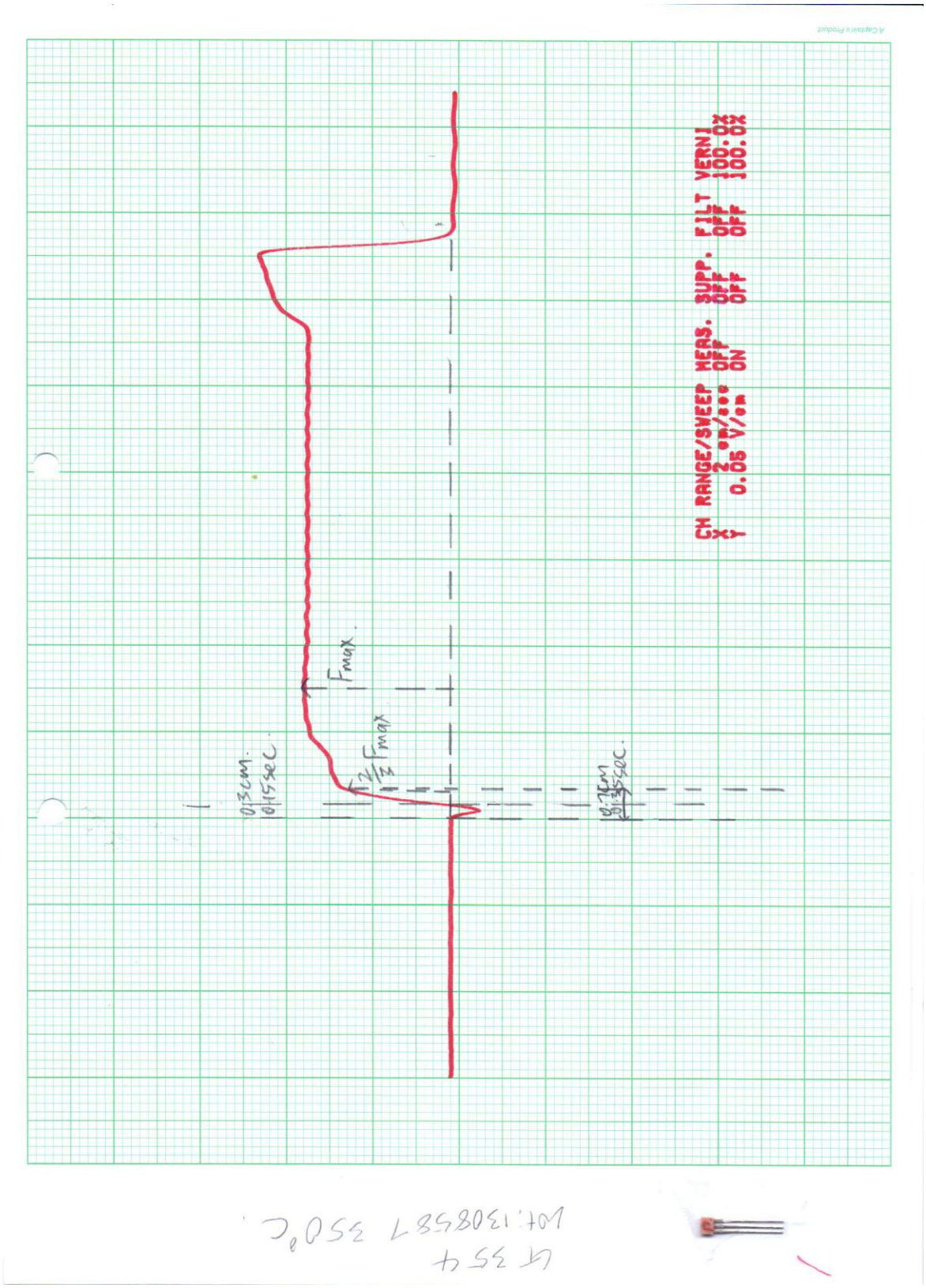

Figure 13: Wetting balance curve for leaded IC component on G354 solder alloy at 350^{O}C

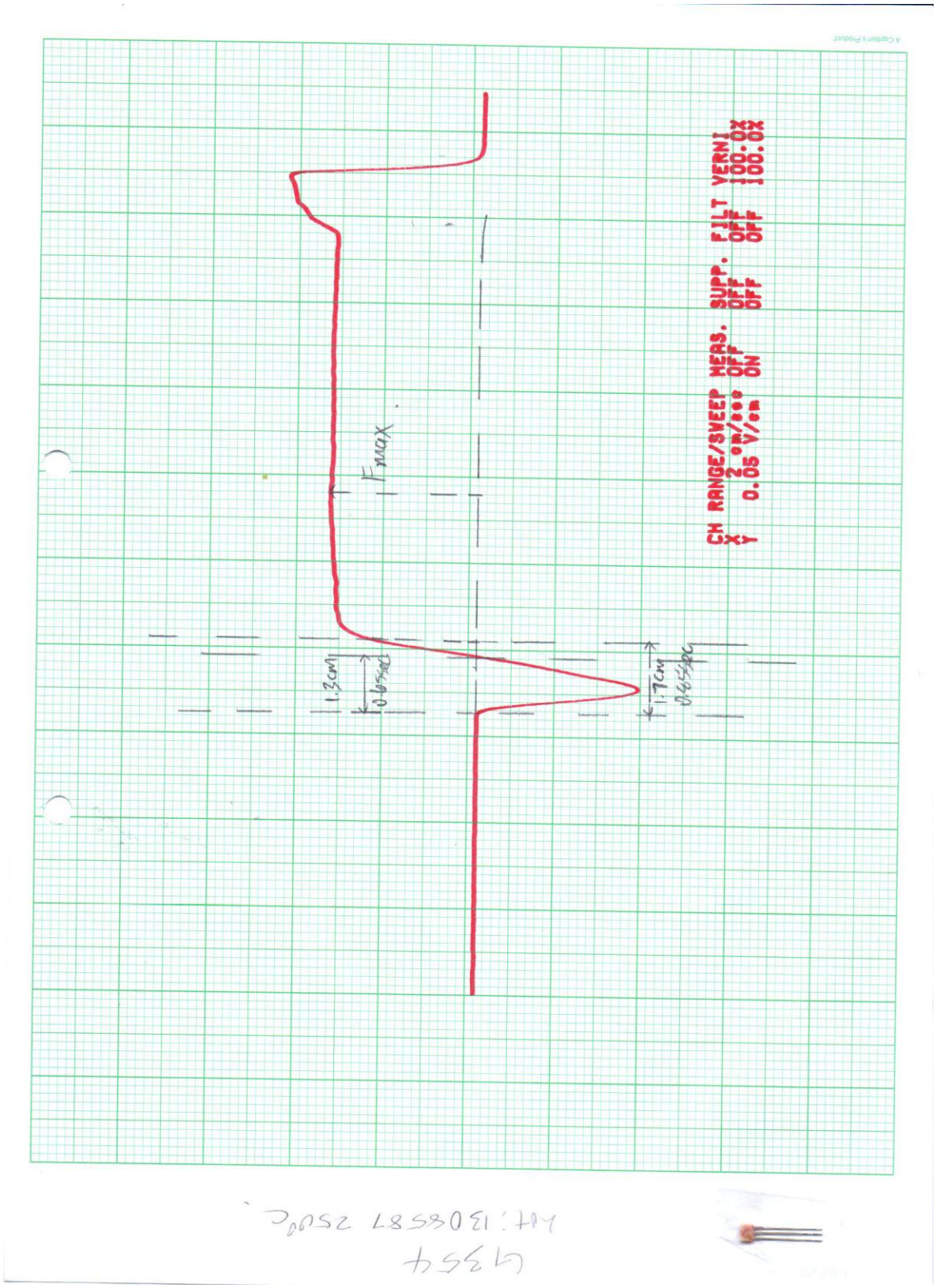

Figure 14: Wetting balance curve for leaded IC component on G354 solder alloy at 250^{O}C

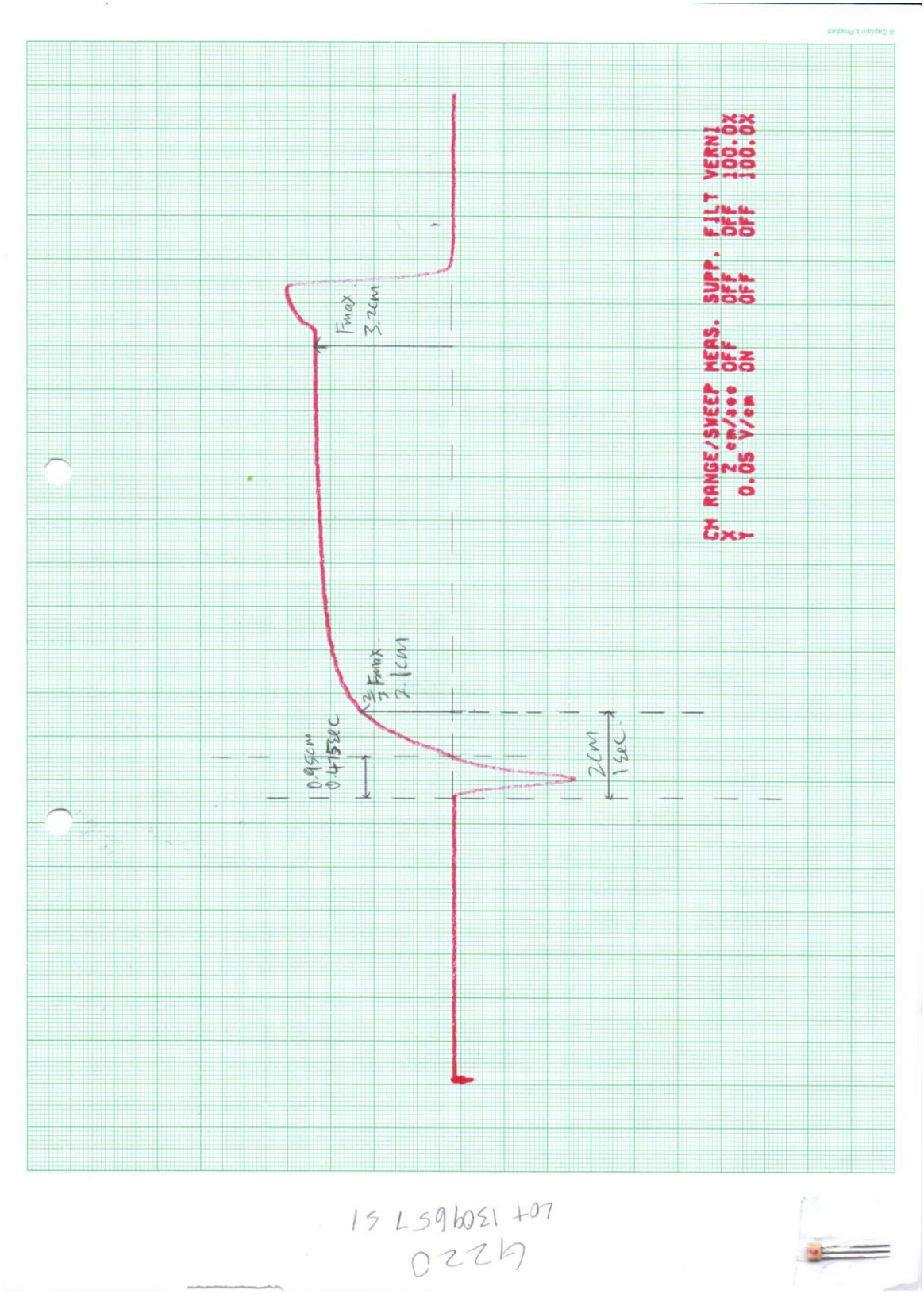

Figure 15: Wetting balance curve for leaded IC component on G220 solder alloy at 250^{O}C

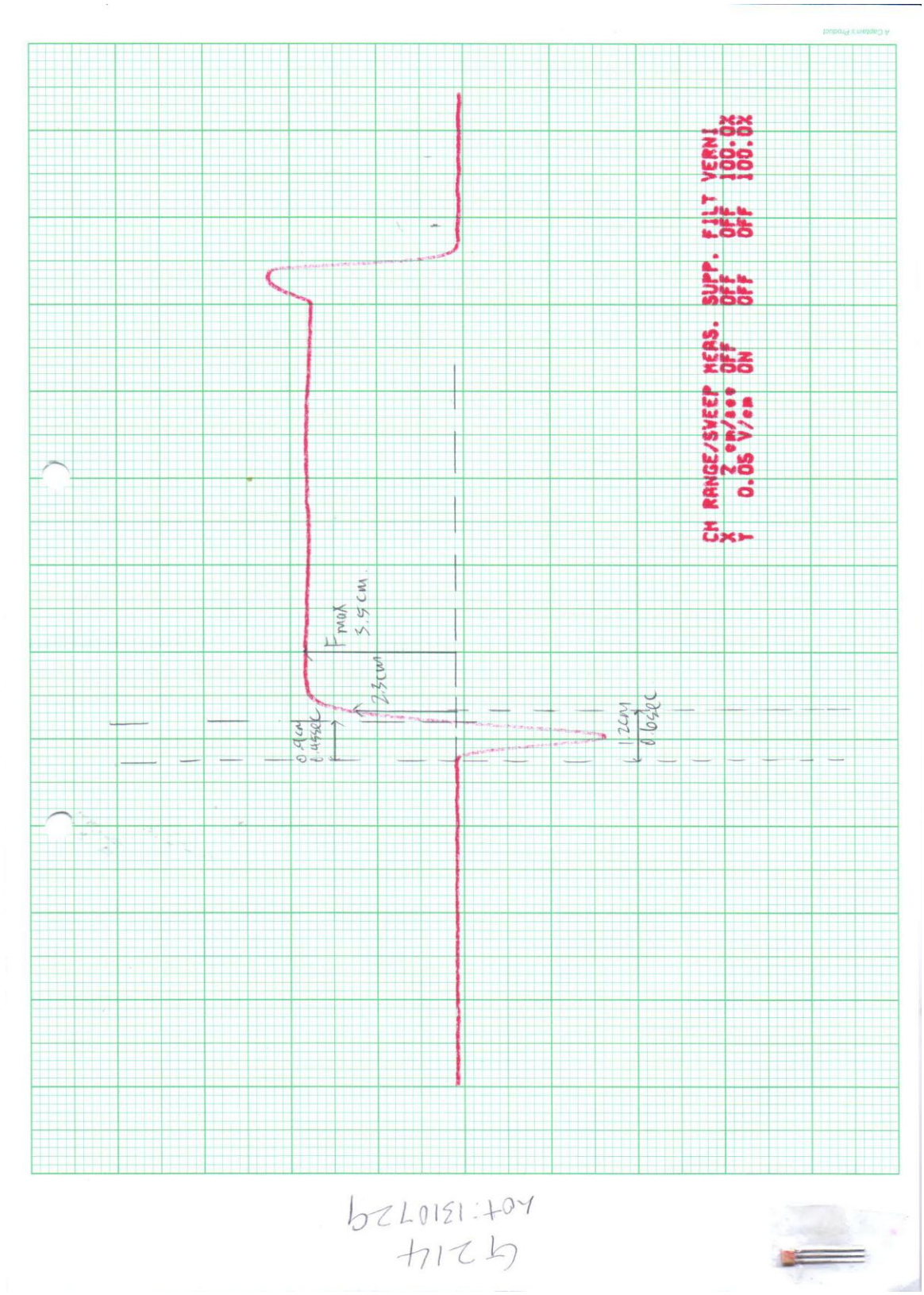

Figure 16: Wetting balance curve for leaded IC component on G214 solder alloy at 250^{O}C

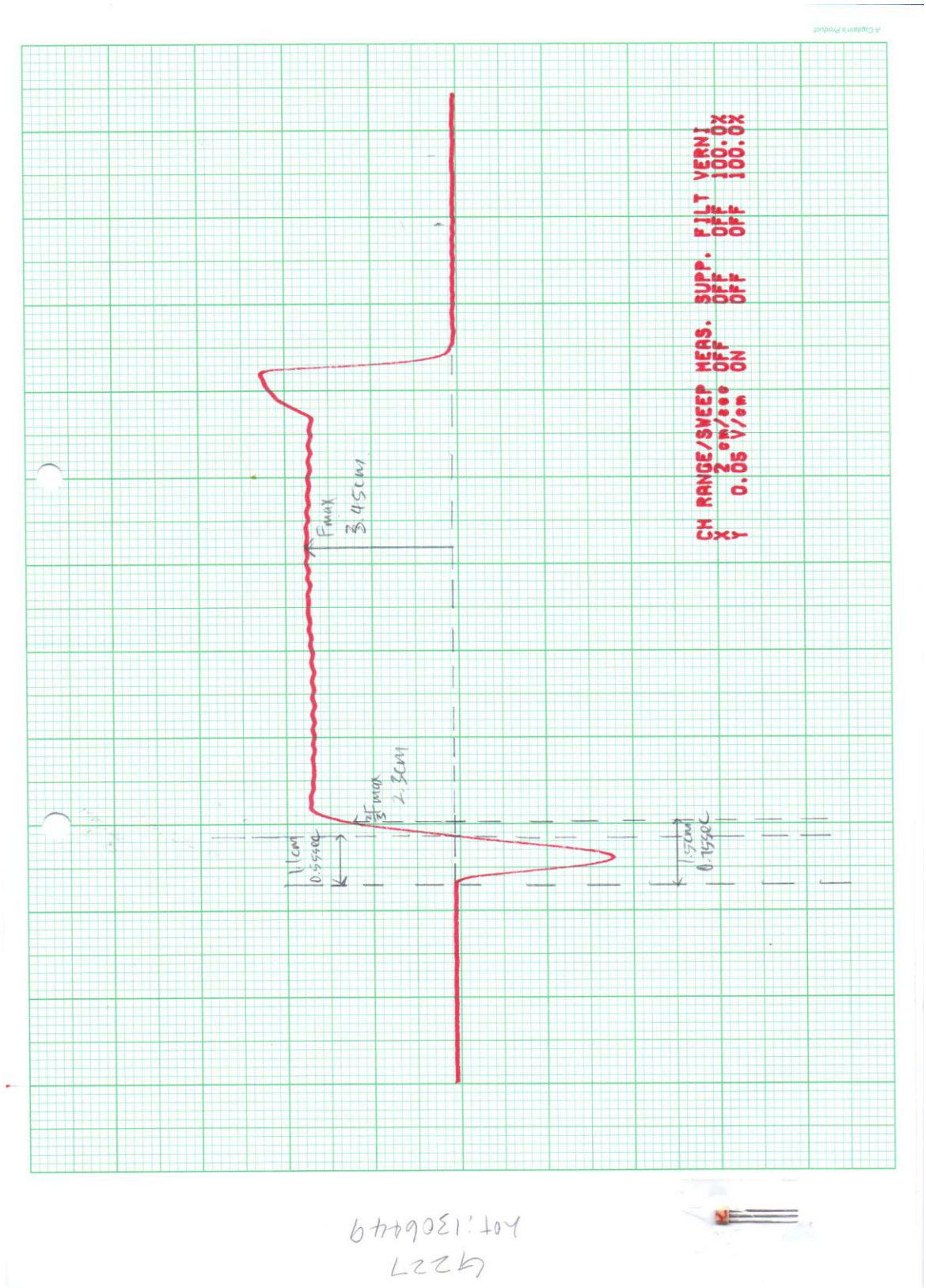

Figure 17: Wetting balance curve for leaded IC component on G227 solder alloy at 250^{O}C

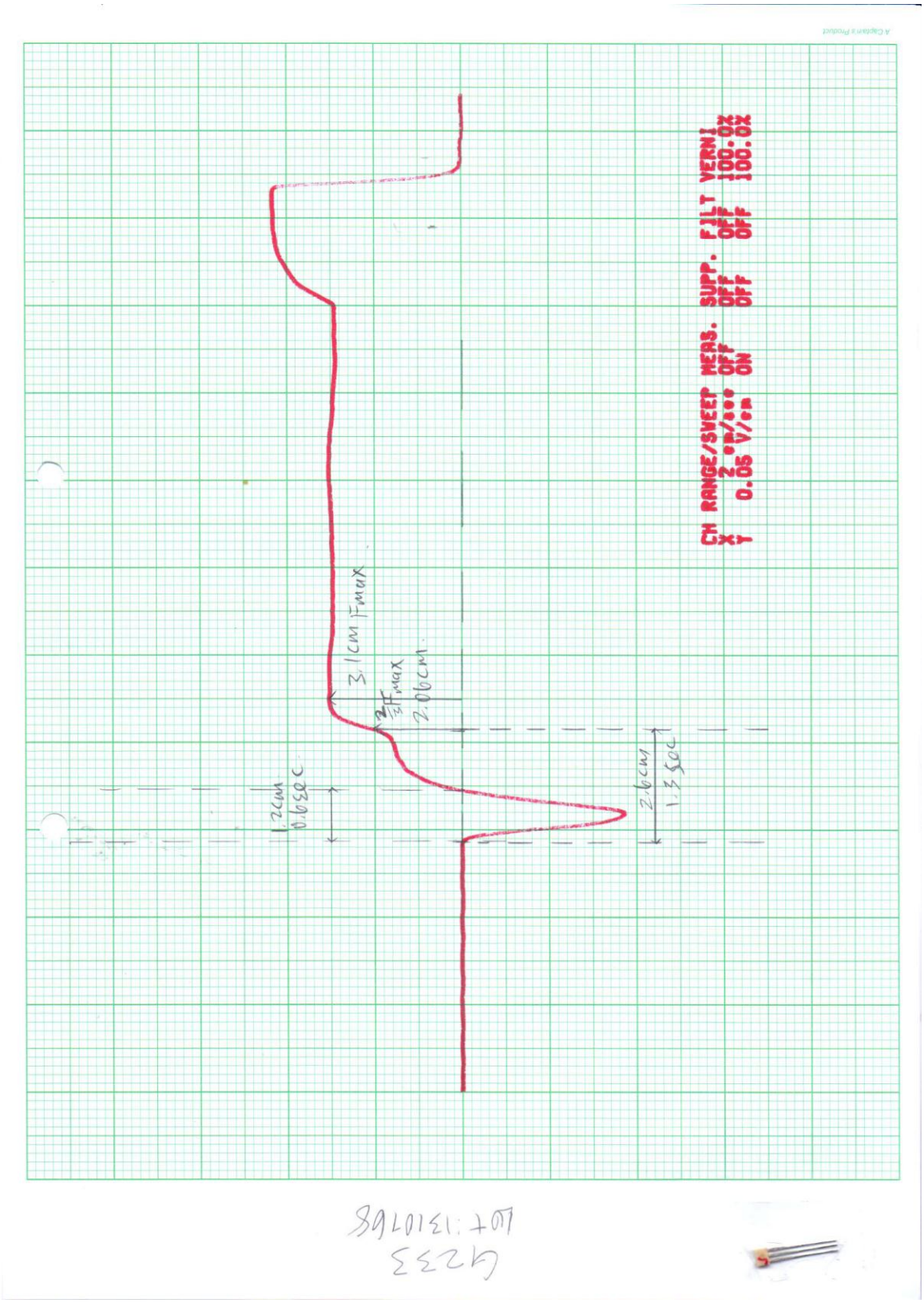

Figure 18: Wetting balance curve for leaded IC component on G233 solder alloy at 250^{O}C